Published Monthly. Price, $5.00 per Annum.

THE JOURNAL
OF THE
AMERICAN CHEMICAL SOCIETY.

VOL. XIX.—NO. 2.

FEBRUARY, 1897.

EDWARD HART, Editor, J. H. LONG, THOMAS B. OSBORNE,
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REVIEW OF AMERICAN CHEMICAL RESEARCH 17-28

EASTON, PA.:
CHEMICAL PUBLISHING COMPANY.

Entered at the Post Office, Easton, Pa., as Second Class Matter.

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The Velocity of the Reaction between Ferrous Chloride, Potassium Chlorate and Hydrochloric Acid. By A. A. Noyes and R. S. Wason.

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VOL. XIX. [FEBRUARY, 1897.] NO. 2.

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

SOME PRESENT POSSIBILITIES IN THE ANALYSIS OF IRON AND STEEL.[1]

BY C. B. DUDLEY.

To the analytical chemist, there are few substances in nature, more interesting than a piece of pig iron, few substances which have received more study, and few which present chemical problems more difficult of solution. The amount of work which has already been done in connection with this very common but very complex substance, is something enormous. Indeed, if we add to the study which has already been put on pig iron itself, the work which has been done on what may perhaps fairly be called its progenitors, *viz.*, the ores, the fuel, the flux, and the refractory materials used in its production, and then consider still farther the labor already expended in the analysis of what we may call the progeny of pig iron, *viz.*, castings, wrought iron, malleable iron, and the numerous grades and kinds of steel, made by the various processes of the present day, we shall surely be safe in saying that more chemical work has been done in connection with pig iron, than with any other substance in nature. Is it too much to affirm that at the present time one-third, possibly one-half of all the chemical work done in the world, is in connection with the iron industry, either in the solution of unworked-out problems, the development of new methods of analysis, or in the routine analyses affecting the interests of producer and consumer.

But the amount of work already done and in daily progress in connection with this substance, is not all that may be said in

[1] Presidential address delivered at the Troy meeting of the American Chemical Society, December 29, 1896.

regard to it. The complexity of pig iron is very great, and consequently the analytical problems presented are far from being easy of solution. It may not be uninteresting to enumerate some of the substances which have already been found in pig iron. We find, besides the element iron, carbon, phosphorus, silicon, sulphur, manganese, copper, chromium, tungsten, titanium, vanadium, nickel, cobalt, aluminum, potassium, sodium, magnesium, calcium, and lithium. It is fair to say that there is apparently well grounded belief that the last five are characteristic of intermingled slag, rather than of the metal itself. It is not intended that it should be understood that all of these substances have been found in any one sample of pig iron, but that all these substances have actually been detected in the analysis of this alloy. Indeed there seems no reason why any element, which either occurs in the metallic condition in nature, or which is reducible to that condition by carbon, and which is not volatile at the temperature of the blast furnace, may not occur in pig iron, provided of course it will alloy with the metal. Quite a large number of other substances besides those mentioned above have actually been alloyed with some form of iron or steel. Among these may be mentioned zinc, tin, lead, antimony, bismuth, molybdenum, silver, platinum, rhodium, iridium, palladium, and gold. Nor is this all that may confront the analyst, who devotes himself to the chemistry of iron and steel. Not less than three elements which usually exist in nature in the gaseous form, occur in these metals, and are believed to have important influences on their physical properties. These are oxygen, hydrogen, and nitrogen; while the numerous analyses show the presence of carbon monoxide in both cast iron, wrought iron, and steel. It seems quite evident that the chemist who hopes to successfully cope with the problems which are involved in even the ultimate analysis of iron and steel in their various forms, must be well equipped with a liberal share of the methods and processes known to mineral chemistry, and on the other hand, if he attempt the proximate analysis of these substances, or the separation and determination of the various compounds of the elements present, with iron or with each other, he will at least be brought on the border ground of organic chemistry. Some of the carbon compounds

which are characteristic of the brilliant work of the present president of the French Chemical Society, are known to occur in or have already been isolated from pig iron.

It would lead us too far from our present purpose to do anything more than enumerate the largest number of the elements given above. Suffice it is to say that in what follows, we shall confine ourselves to the five first mentioned ; *viz.*, carbon, phosphorus, silicon, sulphur, and manganese. And the question which we shall ask ourselves is, 'What is the present condition of a portion of the analytical methods for the determination of these substances, considering these methods both in regard to their accuracy and speed?' One word of precaution. It would be manifestly impossible to comment on all the methods in use for determining these constituents. To enumerate them alone would weary your patience. We shall confine ourselves, therefore, principally to methods which may be or are used when the diverse interests of producer and consumer are involved.

Beginning then with total carbon in pig iron, wrought iron, and steel, we deem it safe to say that the method by combustion in oxygen gas, as at present known and worked in many laboratories, leaves very little to be desired, so far as accuracy is concerned, and is sufficiently rapid for most commercial uses. The modification introduced some years ago, of using a solution of the double chloride of copper and ammonium, instead of simple chloride of copper,[1] to release the carbon from the iron, took away from the combustion method, one of its greatest difficulties ; *viz.*, the long time required to dissolve the metal. This modification, as many will doubtless remember, reduced the time required for solution, from two or three days, to an hour or less. Indeed, at the present time, if a good stirring machine is used, it is quite possible to dissolve three grams of fairly fine borings of pig iron, wrought iron, or steel, in 200 cc. of the proper solvent in from ten to forty minutes. Still further the studies of the Committee on International Standards for the

[1] It is difficult to say positively who first suggested this modification. The first mention in literature that we are able to find is in the *Transactions of the American Institute of Mining Engineers*, 4, 157, by J. B. Pearse. But a private communication from Andrew S. McCreath, states that he made the suggestion while working under Pearse, and that Professor Richter, in the Leoben Jahrbuch, had previously suggested the use of potassium or sodium chloride with copper chloride, which led him to try the ammonium salt. McCreath's description of the method as used by himself, is published in the *Transactions of the American Institute of Mining Engineers*, 5, 575.

Analysis of Iron and Steel, have further modified the method, and it is believed rendered it much more accurate. Among these modifications may be mentioned the use of an acid instead of a neutral or basic solution of the double salt to dissolve the metal. This point was thoroughly worked out by Blair.[1] Following this came the work done in the laboratory of the Pennsylvania Railroad Company,[1] demonstrating the unreliability of the use of the double chloride of copper and ammonium as a solvent, owing, as appeared later, to the probable presence in all ammonia and its salts, obtainable in the market, even those marked "C. P.," of some carbonaceous material, possibly pyridine,[2] derived from the gas liquor used in making the ammonia. The substitution of the potassium,[2] for the ammonium salt, has apparently completely overcome this difficulty, and this with the use of oxygen gas instead of lead chromate, in which to burn the carbon, and some modifications of the absorbing and purifying train,[3] have seemingly placed the dry combustion method for determining carbon in the front rank of successful and accurate analytical processes. The principal known source of error in the method at the present time appears to be in connection with the weighing. The potash bulbs and small calcium chloride tube used in absorbing the carbon dioxide weigh, altogether, some fifty to sixty grams, and present considerable surface. If now, between the weighing before the combustion and the weighing after the combustion, the interval being an hour, or a little more, there is considerable change in the hygroscopic condition of the atmosphere, an error of 0.01 per cent. may be easily introduced. If we may trust our experience, it is difficult to make closely agreeing duplicate combustions in showery weather. Blair suggests a method of overcoming this difficulty consisting in having a second potash bulb and calcium chloride tube of, as nearly as possible, the same size on the opposite end of the balance when weighing.

In regard to the accuracy of the method as at present understood, it may be said, that undoubtedly the best test of the accuracy of a method, is the recovery of a known amount of any substance added to the material to be analyzed. This proce-

1 *Trans. Am. Inst. Mining Eng.*, 19, 614.
2 *Trans. Am. Inst. Mining Eng.*, 20, 242.
3 This Journal, 15, 448.

dure being manifestly impossible in the case of iron and steel, we are compelled to judge of the accuracy of the combustion method, as applied to these metals, in some other way. For this purpose, however, we have at hand the results obtained by different chemists, using different methods, but working on the same samples. In the course of the work done by the Committee on International Standards for the Analysis of Iron and Steel, the carbon in four samples of steel was determined, First, by using acid double chloride of copper and potassium as solvent and burning in oxygen gas; Second, by using the same solvent and burning in chromic acid solution; and Third, by treating the borings direct with bisulphate of potash and heat, conducting the carbon monoxide and sulphur dioxide formed over hot solid chromic acid, which oxidized both gases and retained the sulphur trioxide formed, and finally measuring the volumes of the resulting carbon dioxide in an eudiometer tube. Each method was used by a different chemist. The results obtained are as follows, the letters at the side representing the four samples of steel, the figures at the top representing the chemists, and the figures in the columns the percentages of carbon in the steel samples:

	1.	2.	3.
A.....	1.455[1]	1.440[1]	1.450[2]
B.....	0.815	0.800	0.815
C.....	0.450	0.450	0.448
D.....	0.152	0.185	0.168

The agreement of the results on the first three samples is quite marked. The discrepancy on the fourth sample has not been explained. The matter is discussed in considerable detail in reference 1, but we think it safe to conclude that so far as method goes, the determination of total carbon in pig or cast iron, wrought iron and steel, is reasonably accurate.

The speed of the combustion method as at present worked in good laboratories is quite remarkable, compared with the possibilities twenty-five years ago. A sufficient supply of sample borings being at hand, one operator using two furnaces, may readily make from fourteen to sixteen combustions in a day of eight hours, it being understood that the bulbs are weighed with

[1] *Proc. Eng. of Western Penna.*, 9, [9], 35.
[2] *Ztschr. anorg. Chem.*, 4, [3] und [4], 505.

oxygen gas in them instead of air, and that the last weight of each combustion, except the last one at night, is taken as the first weight of the succeeding one. It is, of course, assumed that when turning out the amount of work above described, the furnaces and apparatus are all in good order, and everything working well. Accidents, an occasional overhauling of the apparatus, blank combustions from time to time for testing purposes, and once in a while an obstinate steel that refuses to dissolve in time or gives trouble in filtration, will all tend to diminish output. The results obtained with this rapid work show, when duplicates are made, occasional discrepancies as high as three hundredths of a per cent. in a steel containing one per cent. of carbon, but we have seen very large numbers of duplicates, made as above described, which did not disagree one one-hundredth.

Again, when work is not so plentiful as to admit of the procedure described above, the method still permits satisfactory speed. Starting with a fresh sample of borings and everything in good order, but cold, it is not difficult to get two closely agreeing determinations on the same sample in two hours and a half. Of course, in investigation or referee work, more time would undoubtedly be used, especially if the interests involved are very great. But we have many times been astonished in our own laboratory, at the close agreement between the results obtained in the rapid manner described above, and the duplicate analysis made on the same sample for confirmatory purposes, but using much more time and pains.

Turning now to the determination of combined carbon and graphite, we do not find the state of affairs so satisfactory. As is well known, these two constituents are usually found by first determining total carbon, then dissolving another portion of the sample in hydrochloric acid, filtering and washing with caustic potash, alcohol, and ether, and then burning the residue, collecting and weighing the carbon dioxide formed, as in an ordinary combustion. The result is called graphite, and the combined carbon is the difference between the total carbon, and the graphite. But as Shimer[1] has so well shown, what we actually get by this procedure is not necessarily the graphite and the

[1] *Trans. Am. Inst. Min. Eng.*, 25, 395.

total combined carbon in the sample, but only the combined carbon which exists in the metal as a carbide soluble in hydrochloric acid. If the sample contains carbides not soluble in that acid, nor in the materials used in washing, the carbon of these carbides appears with and is counted as graphite. Shimer shows that titanium, and possibly vanadium carbide, are apparently not infrequently thus counted. The use of sulphuric instead of hydrochloric acid leads to the same error, while the employment of nitric acid as solvent, apparently gives the graphite much more definitely, but leaves us in doubt as to whether the combined carbon is really the combined carbon which we want, in order to have light on the quality of the metal we are dealing with. It is obvious that the difficulty here is in our lack of knowledge as to what carbides actually exist in pig and cast iron, and if there are several of them, which one or ones do we actually want to know the carbon content of. If we knew positively that the combined carbon wanted was that which exists in the metal as carbides of iron and manganese, and that these carbides were soluble in hydrochloric or sulphuric acid, while all other carbides present were not soluble in these acids, obviously we should use these acids when determining combined carbon. On the other hand, if we want to know only graphite, and care little about the combined carbon, apparently nitric acid is the solvent to use. It is clear that much more work is needed on this subject, a state of affairs which as we progress, we shall find is characteristic of other constituents of the metals we are considering.

Much might be said in regard to the color test for determining carbon in steel. It is difficult to over-estimate the value and importance of this method, especially in the daily operation of steel works, and there seems little doubt but that if proper precautions are employed, the method in skillful hands will give results that are fairly reliable to within three or four-hundredths of a per cent. It would hardly be possible in this paper to discuss all the precautions which are deemed essential by those best informed. A chemist of wide experience with the method, has enumerated twenty-four points that must be observed, if reliable results are to be expected. Let it suffice for us to say that even approximate accuracy cannot be expected.

1. If the steel whose carbon is to be determined and the standard steel do not have their carbon in the same condition. For example, if the standard steel has been annealed, and the sample to be tested has been tempered, the results will be worthless.

2. If the attempt is made to determine the carbon in any steel by using a standard widely different from it, in carbon content. Using a 0.20 per cent. carbon standard, with a steel containing 0.50 or 0.60 per cent., is apt to lead to very fallacious results.

The best results seem to be obtained by having the carbon in all steels both standards and tests in the condition given by annealing, by having a number of standards which differ little from each other in carbon content, and by not attempting to use the method on steels containing very little or very large amounts of carbon. It may not be amiss to add here that the practice so prevalent in many of the steel works, of using this method for all carbon determinations, including those where contracts are involved, is reprehensible and should be discontinued. The chemist at the works does the best he can with the method he is using, and the amount of work required of him, as well as the facilities furnished, do not admit of the use of a better method. On the other hand when a dispute arises, and it is ultimately shown that the works are in error, the chemist is blamed and analytical chemistry brought into disrepute, not because either is really at fault, but because more is expected of the color test method, than it is really able to give. To the steel makers we say, "Do not expect your chemist to render you the bricks of good chemical analyses, without you give him the requisite straw of time and appliances to do good chemical work."

Few of the constituents of iron and steel have more important influences on their valuable qualities than phosphorus, and upon few has more chemical work been done. The present condition of the methods for determining this constituent, seems fairly satisfactory provided we are willing to take time enough to do the work. In confirmation of this statement, the work[1] done by the Sub-committee on Methods of the International Committee on Standards for the Analysis of Iron and Steel may be cited. This sub-committee consisted of five members, each of whom analyzed five samples of steel, and each used his own method, without any

[1] *Proc. Am. Soc. Civil Eng.*, 21, 59.

attempt at consultation or agreement with each other before the work was done. The methods employed may be briefly indicated as follows, those interested being referred to the report of the committee published as per the reference given for the details. Mr. Blair used what is known as the acetate method. Mr. Shimer used the molybdate magnesia method. Your speaker used a combination of the acetate and molybdate magnesia methods. Dr. Drown used a combination of certain features of the modern rapid methods with the molybdate magnesia method. And Mr. Barba on one sample used the acetate method as described by Blair, and on the other four samples employed certain features of the molybdate method to separate the phosphorus from the iron, and then used the reductor to get the amount of phosphorus, instead of weighing as magnesium pyrophosphate. It will be evident to any one carefully reading the report referred to, that the methods employed differed widely in principle, in strength of solutions, and in manipulation, and yet these methods gave the following percentages of phosphorus in the five samples:

	1.	2.	3.	4.	5.
Mr. W. P. Barba.....	0.041	0.015	0.095	0.091	0.041
Mr. A. A. Blair	0.040	0.016	0.098	0.091	0.041
Dr. T. M. Drown	0.042	0.016	0.104	0.090	0.042
Dr. C. B. Dudley	0.040	0.016	0.099	0.097	0.039
Mr. P. W. Shimer....	0.041	0.017	0.098	0.096	0.039

In explanation of the results, we quote from the report of the sub-committee.

"Sample No. 1 is an ordinary open-hearth steel. Sample No. 2 is a crucible steel. Sample No. 3 is an open-hearth steel to which metallic arsenic was added while in the molten condition in a crucible. Sample No. 4 is an ordinary Bessemer rail steel. Sample No. 5 is the No. 5 sample of the Committee on International Standards, and is an open-hearth steel.

"It will be observed that the agreement in the results on phosphorus obtained by the different chemists is very good. The exceptions are the No. 3 steel, which contains arsenic in considerable amount, and where the discrepancy is 0.009 per cent., and in the No. 4 steel, where the discrepancy is 0.007 per cent. Considerable work was done on the No. 4 sample, in an effort to reconcile discrepancies, and it was found that the turnings from this

sample were irregular, and that two different bottles of the sample gave different results. The average of six determinations from one bottle was 0.1057, and the average of five determinations from another bottle was 0.0964 per cent. Furthermore, siftings from quite an amount of the turnings gave 0.140 per cent."

But these methods are long and laborious. It would be impossible with the most rapid of them to get a result in much less than a day, while two days would certainly be required for some of the others. Accordingly, since the demand for rapid phosphorus determinations during the last ten or fifteen years has been very great, an enormous amount of work has been done in trying to meet this demand. Modification after modification has been introduced, and paper after paper published on the subject. It is perhaps not too much to say that few chemical journals that publish any original work at all, have escaped three or four articles per year, on the determination of phosphorus in iron and steel, or on some phase of a rapid method for such determination. The result of all this work has apparently been constantly increased rapidity, with constantly greater approximations to accuracy. The present state of the matter is perhaps best shown by Thackray[1] in his paper, "A Comparison of Recent Phosphorus Determination in Steel." This writer sent to some twenty-three different chemists borings from two different samples of steel, with a request to have the phosphorus determined in each sample, and a description of the method used sent with the results. Each chemist was told that samples had been sent to others, but no attempt was made to have any special method used. The chemists embraced a professor in a technical school, the chemist of a large consumer, a number of commercial chemists, and a number of chemists employed by steel and iron works. On one sample thirty-six different results were sent in, and on the other thirty-eight. Twenty-seven different methods were employed, some of the chemists sending in results by two, and even three methods, and some sending duplicate determinations. The results obtained were obtained as follows, the figures being percentages of phosphorus in the steels:

[1] *Trans. Am. Inst. Min. Eng.*, 25, 370.

Sample.	1.	2.
Average of all determinations	0.0496	0.0835
Highest result	0.055	0.091
Lowest result	0.045	0.076
Maximum difference	0.010	0.015

The methods employed may be divided on the basis of time required into three classes:

1st. Those which may be called rapid, and which give a result in two hours or less.

2nd. Those which may be called slow, and which require considerably more than two hours, but still give a result the same day.

3rd. Those which may be called very slow, and which do not give a result until the second day or later.

Thirteen results on each sample were given by "rapid" methods, eleven on the No. 1 sample, and twelve on the No. 2 sample by "slow" methods, and twelve on the No. 1, and thirteen on the No. 2 by "very slow" methods. Arranging the results in accordance with this classification of the methods (and we have some very interesting data), the figures being as before, the percentages of phosphorus in the two steels are:

	Rapid methods.		Slow methods.		Very slow methods.	
	1.	2.	1.	2.	1.	2.
Average of all determinations	0.0499	0.0840	0.0490	0.0826	0.0496	0.0837
Highest result	0.054	0.091	0.052	0.086	0.055	0.089
Lowest result	0.045	0.078	0.046	0.076	0.046	0.078
Maximum difference	0.009	0.013	0.006	0.010	0.009	0.011

To our minds these figures are very impressive. It is worthy of note—

1st. That the average results given by the "rapid" methods only differ on either steel from the averages given by the "slow" or "very slow" methods, by a little over 0.001 of a per cent.

2d. That the maximum difference between the highest and lowest results given by the "rapid" methods on either steel is but a trifle greater than is shown by the "slow" or "very slow" methods.

In other words, if we interpret these results correctly they show that the rapid methods for determining phosphorus in steel now known and in use in many laboratories give results that are well nigh as accurate and reliable as those yielded by the longer and more laborious methods, and it must not be forgotten that

although we have placed two hours as the time characterizing a rapid method, a number of the results given above were obtained by the use of methods which give a single determination in forty-five minutes, and enable one operator to make twenty phosphorus determinations in a day. We are frank to say we do not believe such a showing would have been possible five years ago.

But these results still leave something to be desired. The discrepancy between the highest and the lowest result, is still too great. It is, perhaps, a little hazardous to place limits, but we do not think the chemists of the country should be satisfied until they are in possession of a method or methods which are so carefully worked out and so well described that in the hands of different chemists of good, fair ability and experience, results will be obtained by all, when working on the same steel, that will not differ from each other more than 0.003 per cent. The Sub-committee on Methods of the International Committee on Standards for the Analysis of Iron and Steel before referred to, have had in hand now for some two years, studies on a rapid and accurate method for the determination of phosphorus in steel. It has been the hope of the sub-committee that the ideal above given would be attainable by this method. In reality, the work of the sub-committee has embraced an examination of almost every chemical point involved, taking very little if anything for granted, and checking and proving every step. The work is not yet quite ready for publication, one or two points remaining which are not entirely settled, and it has been deemed advisable to withhold the method until these are completely cleared up.

Some years ago, with the publication[1] of what is commonly known as Ford's method, the determination of manganese took a decided step forward, at least in this country, so far as speed is concerned. Previous to that time the long and laborious acetate method which involved the separation of the iron from the manganese as basic acetate and subsequent precipitation of the manganese by means of bromine or as pyrophosphate, had held full sway. Ford's contribution consisted, as is well known, in separating the manganese from hot nitric acid solution of the iron or steel, by means of potassium chlorate, and Williams[2]

[1] *Trans. Am. Inst. Mining Eng.*, 9, 397.
[2] *Trans. Am. Inst. Mining Eng.*, 10, 100.

added the modification, now in common use, of determining the separated oxide of manganese, by its action on a standard solution of ferrous sulphate or oxalic acid. This method as now worked in many laboratories, gives a single result in forty minutes and two in an hour, and enables one operator to turn out twenty to twenty-five determinations in a day. The accuracy of this method has been questioned. We are not aware of any recent symposium on manganese, where different chemists using different methods, have worked on the same steels. In our hands this method gives results closely agreeing with check work done by the more laborious and generally accepted accurate methods, provided the sample contains not more than three-fourths of a per cent. On samples containing over one per cent. of manganese, the results are apt to be low, owing probably to the fact that the manganese does not separate from the nitric acid solution as manganese dioxide, but as some other oxide, whose composition is not positively known. In the calculation it is customary to regard the separated oxide as manganese dioxide, and this leads to perceptible error on large amounts. Producers and consumers rarely contend much over manganese in steel, and methods for its determination have perhaps not received, on that account, all the attention they deserve. There is evident need of more work on this subject.

The methods for the determination of silicon can hardly be regarded as in a perfectly satisfactory condition. If evaporation to dryness to render silica insoluble, is employed, the time required is considerable. If dehydration by means of sulphuric acid and heat, as suggested by Drown[1] is employed, there are difficulties which interfere somewhat with accuracy. There seems little doubt, but that in skilled hands, with sufficient care taken in the manipulation, a couple of determinations may be made on the same sample, using Drown's method, that will agree closely with each other, and with results given by the longer and more laborious methods. On the other hand, where one operator is making a number of determinations at the same time, there is much danger of error, due either to failure to dehydrate sufficiently or to overheating, resulting in the formation of insoluble iron salts. Our experience indicates that the margin between

[1] *Trans. Am. Inst. Min. Eng.*, 7, 346.

these two extremes is not very wide, and that it is fully as frequent to have duplicates on the same sample disagree as to agree. Our observations point to the view that the difficulty of insufficient dehydration is due to the separation of iron salts, as the sulphuric acid concentrates. These salts enclose gelatinous silica, and prevent the dehydrating acid from getting at it. Unless great pains are taken, therefore, to secure this contact by sufficient stirring, the results will be low. If by some modification the iron salts could be kept in solution until the silica is rendered quite insoluble, it would apparently be a decided step forward with this method. It may not be amiss here to call attention to the fact first noticed in the laboratory of the Pennsylvania Railroad Company,[1] that after the dehydration and subsequent dilution are finished, if an interval of a few hours is allowed to elapse before filtration, the silica will redissolve and the results be low. Apparently as we are able to work the method, the silica is not completely dehydrated, but only sufficiently so that if filtered at once, fairly accurate results will be obtained.

It is difficult to say anything positive about the speed and output of Drown's method. It is probably safe to say that a couple of determinations could be made in an hour and a half, but, on account of the difficulty mentioned above, the method does not lend itself well to working on a large number of samples at once, and consequently a large daily output is somewhat interfered with.

It must also be said of the methods for the determination of sulphur in iron and steel, that those most in use are hardly as satisfactory as could be desired. The studies of Phillips[2] conclusively show that when using the evolution method, the whole of the sulphur content is not given off in such a form as to be retained by the usual means employed to catch the gas. It seems not too much to say that it is hazardous to use the evolution method on pig or cast iron, even when fusion of the residue is employed. The formation of unoxidizable gases containing sulphur, in the application of the evolution method to steel, has

[1] Address to the members of the Chemical Section of the Engineers' Society, at Pittsburg, September 27, 1892, by C. B. Dudley, on "Discrepancy in Chemical Work by Different Workers."

[2] This Journal, 17, 891.

not, so far as our knowledge goes, yet been demonstrated, and accordingly the evolution method is still used largely on steels. But on pig and cast irons the oxidation method seems the only one applicable and some recent studies of Blair, described in a paper at this meeting,[1] indicate that on certain pig irons, all the sulphur is not given, even by this method, unless the graphitic residue is fused with sodium carbonate and niter. Both methods are somewhat slow, and there is need of further study. If some means could be found by which barium sulphate could be readily and accurately converted into sulphide so that a volumetric method could be applied to this sulphide, it would be a decided step forward. The necessity in accurate work for purifying barium sulphate, as first obtained from almost any solution, by fusion and reprecipitation, adds quite considerably to the time required. With steels and two sets of evolution apparatus, using bromine for oxidation, two determinations may be made in two hours With four sets of evolution apparatus, one operator can make twelve determinations in a day. In these cases purification by fusion is not attempted. By the oxidation method on pig or cast iron, two determinations require about five hours, while one operator with a supply of borings ahead and sufficient appliances, can get from ten to twelve results in a day. With this output, purification by fusion is not attempted. If this is done, the time for a pair of determinations must be extended an hour and a half, and the daily output would be cut down at least a third.

From what has preceded in this hasty and necessarily imperfect survey of a portion only of the analytical methods in use in the iron and steel industry, it is clearly evident that there still remains an enormous amount of work to be done in connection with methods. We have touched upon only five of the fifteen or twenty constituents occurring in and affecting the quality of iron and steel, and find the methods for determining even those more or less imperfect, and needing more work. What will be our condition as chemists if, as seems probable, nickel, chromium, aluminum, tungsten, and the gases, oxygen, hydrogen, and nitrogen, either free or combined, within the next few years, come into prominence as constituents of iron and steel, and are made elements in important commercial contracts? Still further, thus

[1] See page 114 of this issue.

far our methods are concerned almost entirely with the total content of the various constituents we are determining. We know very little about the compounds of the various constituents occurring in iron and steel, with the metal or with each other. Is the phosphorus present as phosphide or phosphate, or both? How besides as sulphide does the sulphur occur? Do the various carbides which are revealed by the microscope, and which are believed to be so closely dependent on the heat treatment which steel receives, and which are so intimately related to the value of the metal, differ from each other in carbon content, or only in crystalline form? Who will be the first to isolate any of these carbides? Who will first give us a practicable, accurate and sufficiently rapid method for determining oxides in steel? Who will first completely investigate the relation between the chemistry and the chilling properties of cast iron? And who will first give us a study on the form in which nitrogen occurs in this metal, and a sufficiently rapid and accurate method for its determination? Truly the harvest of chemical work before us in connection with iron and steel is bounteous. Will the laborers be forthcoming to gather the harvest?

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CINCINNATI.]

XLIX. SOME PECULIAR FORMS OF IRON.

BY T. H. NORTON.

Received January 18, 1897.

I HAVE recently had occasion to examine two rather odd forms of iron, the peculiarities of which are sufficiently marked to warrant a brief note. The first of these is a sample from a mass of pig iron taken from a deep crevice in the hearth of a blast furnace at Ætna, Tenn., after the furnace was blown out. The conditions were such that the iron had been maintained in the molten condition for over a year, and had then cooled and solidified very slowly.

In appearance the sample is of a light, silvery color, and exhibits a most marked crystalline structure, with rectangular cleavage. Despite this crystalline character, it is the reverse of brittle, and shows a high degree of malleability, fragments being easily flattened out with a hammer. The drill makes but slight

impression on it. Portions were tempered and then the attempt was made to pulverize them; a slight crumbling was manifested at first, but after a few strokes of the hammer they became perfectly malleable. The piece could be split easily with a chisel, especially along the lines of cleavage. Small cubical fragments detached by this means and hammered out so as to form very thin plates, were used as material for analysis, as drillings could not be secured. Even in this form, solution was effected very slowly.

Manganese was determined by Volhard's titration method; silicon by Drown's method; sulphur by the cadmium chloride method followed by titration with iodine; phosphorus by Handy's method; and carbon by the Dudley and Pease standard method. The following results were obtained:

	Per cent.
Manganese	0.0362
Silicon	0.0262
Sulphur	0.0106
Phosphorus	0.8285
Carbon	0.1035

It will be seen that the sample would be nearly pure iron, but for the phosphorus present, this being the only serious impurity. It is probable that the peculiarities above noticed are due to this unusual combination, although the very slow cooling may have influenced the crystalline condition.

The second specimen is the result of the prolonged action of the inner part of a non-luminous Bunsen flame on ordinary steel. It has served to support the mantle of an Auer von Welsbach lamp, which has been in steady use for two years, and has been exposed during this period to the combined action of a high temperature and the gases of the inner cone of the flame. As a result it has become so brittle that the upper half crumbles as easily as chalk. The lower portion, less exposed to the flame, is covered with a brittle layer, while the central core is still pure steel. Carbon determinations by the Dudley and Pease method were made of both the original steel and the brittle portion. The latter, although finely divided, required nearly a week for complete solution. The figures obtained were:

	Original steel. Per cent.	Altered portion. Per cent.
Carbon	0.6423	0.0978

About six-sevenths of the carbon had disappeared. Whether this loss alone can account for the peculiar structural change in the steel would seem doubtful.

I am indebted to Mr. B. R. Haile for assistance in the above analyses.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CINCINNATI.]

L. A TUNGSTEN-IRON ALLOY.

BY T. H. NORTON.

Received January 18, 1897.

THE nature and composition of tungsten-iron alloys has formed the subject of several papers published during the past few years. As an additional contribution to the literature of the subject, the following brief note of the examination of a commercial alloy may be of interest.

The alloy in question was introduced commercially on account of its extreme hardness. The specimen examined was of a lustrous appearance, except in places where it was coated with a yellowish-green incrustation. A large number of blow-holes were observed. The hardness was about 7, quartz being scratched with some difficulty. The material was quite brittle, being easily shattered with the hammer. The small pieces were powdered with some difficulty in an agate mortar. The specific gravity of the powder was 14.55.

The method of analysis employed was that recommended by Ziegler,[1] which consists essentially in fusion with sodium nitrate in a silver crucible, and subsequent precipitation of the tungsten as mercurous tungstate.

The results obtained were as follows:

	I.	II.
Tungsten	93.22	93.43
Iron	6.08	6.18
	99.30	99.61

Mr. D. M. Roth assisted in the analysis of this alloy.

1 *Ding. poly. J.*, 274, 513.

NOTE ON AN IMPROVED SPECIFIC GRAVITY BOTTLE OR PYKNOMETER.[1]

By Edward R. Squibb.

Received January 11, 1897.

THE first attempt of the writer to improve the ordinary specific gravity bottle was described and illustrated in a paper published in the *Ephemeris*, **1**, 11, for September, 1883, p. 349. The next improvement, wherein the principle of the present bottle was first applied, was described and illustrated in the *Ephemeris* for May, 1884, **2**, No. 3, p. 528. The next improvement was described and illustrated in the *Ephemeris* for July, 1889, **3**, No. 4, p. 1162.

The present form, now to be described and illustrated, has been in use during the past five years with very satisfactory results.

The increasing importance of specific gravity of liquids, and the increasing frequency with which close determinations are required, make any improvement that can be suggested in the apparatus worth describing.

Different authorities give different temperatures, not only for the standard unit water volume, but also a different temperature of the compared volume from the standard volume. The standard volumes most commonly used are 0° C., 4° C., 10°C., 15° C., 15.6° C. = 60° F., 20° C., and 25° C. = 77° F., and it is very convenient to have a single bottle in which the standard water volume can be accurately measured at all these temperatures, and in which liquids can without loss be brought to room temperature for weighing. As the bottles illustrated on p. 113 accomplish these objects easily and accurately they are supposed to be improvements on the older form of bottles.

The control of error by expansion of liquid before weighing has recently been effected by Mr. J. C. Boot in his "New Form of Pyknometer," presented at a meeting of the New York Section of the American Chemical Society, held November 6, 1896.[2] In this bottle change of temperature is controlled by having the bottle made double with a vacuum interspace. But this bottle can be used only at a single standard unit water volume, and the provision by which change of temperature is prevented, also

[1] Read before the New York Section of the American Chemical Society, at the meeting of January 8, 1897.

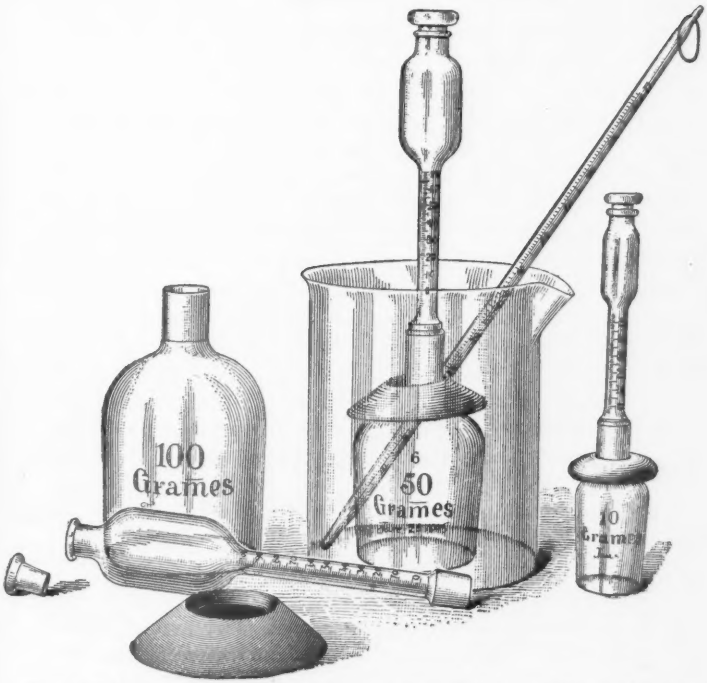
[2] See this Journal, January, 1897, p. 61.

prevents change in adjusting to standard temperature so that this adjustment has to be made before the liquid is put into the bottle, whereas in the improved bottle shown here any temperature of unit volume below 25° C. may be used, temperatures being always adjusted in a bath.

By the adjoining cut it will be seen that the mechanical construction is that of an ordinary thermometer, and as far as temperature is concerned, the principle of action is the same. It therefore has a thin light bulb (the bottle), a graduated stem, and a safety reservoir, the graduated stem being ground into the bottle for facility of filling and emptying. The graduation of the stem is arbitrary, and may be 0 to 50 or 0 to 100.

The use of the bottle and its parts will be easily understood from a description of its adjustment. As received from the glass blower the chemically cleaned and tared bottle should hold say 100 grams of recently boiled distilled water at 20° C. at about fifty-eight divisions of a scale of 0 to 100. In weighing 100 grams of water into the bottle the fine adjustment to 0.001 gram is made by very narrow strips of blotting board that will pass easily down the bore of the graduated stem and absorb minute quantities of liquid. When the 100 grams are in the bottle and the column stands at say 50 to 65 divisions of the scale, the little stopper is put in at the top and the leaden weight is put on the neck, and the whole is immersed in a bath at 0° C. until the column of water in the stem ceases to fall. It should then read at 0 or not much above it and the reading be noted. If it reads below 0 the bottle is too large and the stopper part of the stem must be ground farther into the bottle neck, until the reading on new trials brings the column above 0 at 0° C. Then the bottle is put into a bath at 25° C. and kept there with stirring of the bath until the column ceases to rise, when it should read somewhere from 90 to 100 of the scale. Should it read above 100 of scale, while the lower limit is far above the 0 of scale, then the bottle is too small and the end of the stopper must be ground off until the reading of the column is within the scale at both ends of the scale.

The 100 gram bottle figured in the illustration is one that has been many years in use, and during the first two years the column moved up as it will do in thermometers, but of late



The small stoppers have a minute air passage through the center that could not be shown in the cut.

IMPROVED SPECIFIC GRAVITY BOTTLE, OR PYKNOMETER.

years it has been constant. This bottle has the following scale readings when it contains 100 grams of recently boiled distilled water:

When the column has ceased to move at								4°	C.	the reading is		6.0
"	"	"	"	"	"	"	"	10°	C.	"	"	10.5
"	"	"	"	"	"	"	"	15°	C.	"	"	28.0
"	"	"	"	"	"	"	"	15.6°	C.	"	"	31.0
"	"	"	"	"	"	"	"	20°	C.	"	"	57.5
"	"	"	"	"	"	"	"	25°	C.	"	"	97.5

With such a bottle, specific gravity of liquids can be taken at any of the temperatures of the standard unit volume, to the sixth decimal place. But such accuracy is almost valueless if both

temperatures be not expressed. Fortunately this good practice of always giving both temperatures, as $\frac{4}{4}°$ C., $\frac{15}{4}°$ C., $\frac{15}{15}°$ C., is now becoming common.

THE DETERMINATION OF SULPHUR IN PIG IRON.

By Andrew A. Blair.

Received January 8, 1897.

THERE are two general methods in use for the determination of sulphur in pig iron; the evolution method and the oxidation method. Attention has been repeatedly called to the fact that the residue from many pig irons after treatment with dilute hydrochloric acid contained sulphur, while in some the aggregate evolved as hydrogen sulphide and remaining unacted on in the residue was decidedly less than the amount obtained by the oxidation method. The cause of this discrepancy has been clearly pointed out by Prof. Phillips[1] in his admirable paper on the "Evolution Method for the Determination of Sulphur in White Cast Iron."

Following the line of Prof. Phillips' work I found that it was possible to convert all the volatile sulphur compounds into hydrogen sulphide by passing the evolved gases mixed with hydrogen through a tube filled with pumice and heated to redness. The long boiling that proved necessary and the passage of so much distilled hydrochloric acid and water through the red hot tube made the method too troublesome for ordinary use.

During this investigation I received a sample of pig iron for the determination of its sulphur contents, and used for this purpose not only the oxidation method but the new method as well. The results were as follows:

		Per cent.
1.	Sulphur by oxidation	0.032
2.	Sulphur evolved as hydrogen sulphide	0.000
3.	Sulphur obtained as hydrogen sulphide after passing through red hot pumice	0.005
	Sulphur obtained by fusion of residue	0.057
	Total sulphur	0.062

This seemed to point to the fact that the ferric chloride in the oxidation method held barium sulphate in solution. Mr. P. W.

[1] This Journal, 17, 891.

Shimer made a careful determination of sulphur in this sample by the oxidation method and obtained 0.042 per cent. I repeated all my determinations but the results remained the same. I then made a determination by Bamber's method[1] and found 0.064 per cent. Finally, I fused the residue of carbon, silica, etc., filtered off before precipitating the sulphuric acid in the oxidation method, and obtained 0.030 per cent. sulphur unacted on by hydrochloric and nitric acids. Mr Shimer corroborated these results. In other words, we now have in pig irons :

1. Sulphur evolved, by solution of the iron in hydrochloric acid as hydrogen sulphide.

2. Sulphur evolved as other compounds not absorbed by alkaline lead salts or oxidized by bromine or potassium permanganate.

3. Sulphur in some form, unacted on by boiling hydrochloric acid, but oxidized by nitric acid or aqua regia.

4. Sulphur in some form, unacted on by nitric acid, hydrochloric acid, or aqua regia.

The simplest and most satisfactory method for the treatment of pig irons containing sulphur in the latter form is that of Bamber. It is essentially as follows: Dissolve five grams or a five factor weight (6.878 grams) in strong nitric acid, add two to five grams of potassium nitrate, evaporate to dryness in a platinum capsule and ignite. Treat with water with the addition of a little sodium carbonate, filter, and wash with water containing sodium carbonate. Acidulate with hydrochloric acid, evaporate to dryness, redissolve in water with a few drops of hydrochloric acid, and precipitate boiling with barium chloride.

The pig iron referred to above contains appreciable amounts of titanium and vanadium and Mr. Shimer and I are now engaged in studying the residue insoluble in hydrochloric acid. The results of our investigation we hope will be of sufficient interest to warrant their presentation to the Society.

[1] *J. Iron and Steel Inst.*, *1894*, **1**, 319.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF PURDUE UNIVERSITY.]

THE OCCURRENCE OF RAFFINOSE IN AMERICAN SUGAR BEETS.

BY W. E. STONE AND W. H. BAIRD.

Received January 12, 1897.

THE sugars first noticed in the Australian Eucalyptus manna by Mudie[1] and by Johnston[2] and called melitose[3] by Berthelot; later identified in the cotton seed as gossypose by Boehm[4], and finally in molasses and refinery products of the sugar beet and called raffinose by Loiseau[5], have been shown to be identical with each other. Raffinose has also been found in barley,[6] and in wheat,[7] and is thought to be present in many other plants.[8]

Raffinose, as a distinct kind of sugar, belongs to the not numerous class of tri-saccharides with the formula $C_{18}H_{32}O_{16}$. By hydrolysis, its molecule becomes decomposed, forming one molecule each of dextrose, levulose, and galactose.

Its properties have been thoroughly studied and are probably as well understood as those of most of the more common sugars.

Of particular interest is its occurrence in the residual and secondary products resulting in the manufacture of beet sugar. Here it crystallizes with cane sugar, modifying the crystalline form of the latter and increasing the specific rotation markedly. These two properties actually led to the discovery of raffinose in beet sugar products, where its presence for a long time introduced serious and unexplainable errors into the analytical operations of the sugar factory and refinery.

The frequent occurrence of raffinose in the refinery products from beet sugar, and especially those which have been subjected to any of the methods involving the use of strontia, baryta, or lime for the separation of the sucrose from the uncrystallizable molasses, led to the belief that raffinose was a secondary product derived from sucrose or some other sugar in the course of these

1 *J. de Pharm.*, II, **18**, 705.
2 *J. prakt. Chem.*, I, **29**, 485.
3 *Ann. chim. phys.*, III, **46**, 66.
4 *J. prakt. Chem.*, II, **30**, 37.
5 *Journal des Fabricants de Sucre*, **24**, 52; **26**, 22, etc.
6 O'Sullivan: *Chem. News*, **52**, 393.
7 Richardson and Crampton: *Ber. d. chem. Ges.*, **19**, 1180.
8 Scheibler: *Neue Ztschr. für Rübenzuckerindustrie*, **23**, 237.

operations and that it was not originally present in the beet juices.

It has, however, been conclusively shown that raffinose is a natural constituent of the sugar beet, from which it has been separated directly by Von Lippmann,[1] and the impossibility of any transformation of sucrose into raffinose by heating with alkalies, has been shown by the investigations of Tollens[2] and others.

The quantity of raffinose in beet juice is, however, very small, amounting to from 0.01 to 0.02 per cent. In beet molasses two to three per cent. of raffinose has been observed, and in various concentrated products of molasses refineries, as high as sixteen per cent. has been noted.

Attention has been called to the fact that the amount of raffinose found in sugar beets, is dependent on climate, soil, seed, conditions of growth, etc., and varies between wide extremes. It might, therefore, reasonably be expected that under some conditions this minor constituent of the sugar beet would be lacking entirely.

The conditions under which sugar beets are grown in America must differ in many respects from those of Northern Europe and many of the observations recorded in the latter country may well be subjected to verification here.

On this account it seemed desirable to ascertain definitely whether raffinose occurs in the products of the American beet.

The attention of one of us was called to certain phenomena observed in the works of the Norfolk Beet Sugar Co., at Norfolk, Neb., and an investigation of the same has furnished the data for this paper.

The process of making sugar from beet juices, as carried on at the Norfolk works, involves the following special operations:

After the clarification, concentration, and crystallization of the beet juices, the uncrystallizable residue is returned to the beginning stages of the process and boiled again with fresh beet juice constituting what is known as a "mixed pan."

This is boiled "to grain," *i. e.*, to such concentration that crystals begin to form, and is sent to the "crystallizer," where,

[1] *Ztschr. des Vereins f. Rübenzuckerindustrie*, 39, 880.
[2] *Ztschr. des Vereins f. Rübenzuckerindustrie*, 39, 921.

being slowly agitated under carefully controlled temperature for about twenty-four hours, an increased crop of crystals is obtained. The molasses remaining at this state is treated by the Steffen's process,[1] which consists essentially in precipitating the sugar from a diluted solution of the molasses, by adding finely powdered quicklime at a temperature of 8° to 12° C.

This product consists in the main of mono- and dicalcium saccharates, $C_{12}H_{22}O_{11}CaO$ and $C_{12}H_{22}O_{11}2CaO$.

These saccharates are mixed with fresh beet juices, and boiled in the "clarifiers" and by subsequent carbonation are decomposed. The sugars thus liberated become mingled with a new portion, fresh from the beets. It will be observed that the same particles of sugar, if they fail to crystallize, may repeatedly pass through this cycle of operations, being recovered finally in the form of saccharates and returned to the beginning of the process.

If now we bear in mind that raffinose behaves like sucrose in many respects, especially toward the alkaline earths, with which it forms insoluble compounds, both in hot and cold solutions, we shall readily see how the small amount originally present in the beet juice may accumulate in the molasses and secondary products of the factory. This tendency is increased by the fact that this sugar would, to a large extent, remain uncrystallized in the presence of a much larger proportion of sucrose, and so at the close of the campaign, practically all of the raffinose present in the entire amount of beets which have been handled during the season may be found in the molasses and second grade sugars which are being repeatedly passed through the cycle of operations described.

If, as has been noted, the amount of accumulated raffinose reaches eight to twelve per cent., or even less, it not only destroys the accuracy of all polarimetric determinations of the purity and concentration of the various secondary products of the factory, but also seriously retards the crystallization of the sucrose itself.

For instance, the presence of even two per cent. of raffinose causes an apparent difference in the purity of the molasses sufficient to determine whether it is to be returned to the pan or be

[1] Stammer: Zucker Fabrikation *1887*, 1,047.

sent to the Steffen's process. It is evident, therefore, that successful factory practice may be seriously interfered with if this source of error is ignored.

During the campaign of 1894 and 1895 at the Norfolk factory, it was noticed that the purity coefficient of syrups from the crystallizers, as determined by polarimetric operations, gradually increased, while crystallization seemed to be more and more retarded.

These phenomena could be reconciled with each other only on the assumption of the presence and constant increase of raffinose. Similar observations followed in 1895 and 1896 and it was also observed that the sugar from the crystallizer frequently contained ragged and elongated crystals of abnormal appearance. Frequent inversion tests, according to Creydt's[1] method, indicated the presence of about three per cent. of raffinose, which gradually increased toward the end of the season. On the other hand, attempts to produce mucic acid from the syrups by oxidation with nitric acid, according to Tollen's method, repeatedly failed.

These results, indicating in part the presence of raffinose, seem to render it desirable to undertake the systematic examination of molasses from the "crystallizer," with the object of separating, purifying, and identifying the raffinose, if it should prove to be present. At this time the investigation was transferred to the chemical laboratory of Purdue University.

Renewed attempts to detect raffinose by means of the mucic acid tests were made as follows:

Several ten-gram portions of syrups were oxidized with nitric acid of specific gravity 1.15, according to prescribed methods. Oxalic acid crystallized abundantly from these solutions but no mucic acid could be obtained under these conditions.

Again, to a similar portion of syrup was added so much milk sugar as would yield an amount of galactose equivalent to three per cent. raffinose and this mixture was oxidized in the usual way. This also yielded no mucic acid. The same amount of milk sugar, oxidized in aqueous solution under the same conditions, gave an abundance of mucic acid.

These results illustrate well the unreliability of the mucic acid

[1] *Deutsche Zuckerindustrie*, 11, 757, and 13, 582, etc.

test for raffinose when applied to complex mixtures of salts and organic matters, of which the beet molasses furnishes a good example. Mucic acid was undoubtedly present, as subsequently shown, but was probably held in solution in the form of soluble salts.

Accordingly, steps were taken to separate the sugars in the molasses from other materials with a view of applying the mucic acid test to them directly. This was accomplished by treating about 200 grams of the syrup with an excess of basic lead acetate by which a dense precipitate was thrown down. The liquid was filtered and treated with ammonia until it was strongly alkaline. This produced a second precipitate consisting of lead compounds of sugars. This was filtered, suspended in water, the lead removed with hydrogen sulphide, and the filtrate evaporated to a syrup. To this syrup was added nitric acid of specific gravity 1.15 and the mixture heated in the usual way prescribed in making mucic acid tests.

After three days an abundance of a white crystalline powder separated from the solution, which, after washing and drying, was found to have a melting-point of 213° C., showing it to be mucic acid. This may be regarded as a fairly conclusive qualitative proof of the presence of raffinose in the material studied. Nothing short of the actual separation of sugar in pure form and the determination of its constants, can be accepted, however, as conclusive proof of its presence. Numerous methods have been proposed for the isolation of raffinose from mixtures with other sugars and substances.

Most of these methods are based on the insolubility of raffinose in combination with certain metallic oxides as well as its unusual solubility in absolute methyl alcohol. Following any of these methods, however, its separation is acknowledged to be a tedious operation. Our experience in this attempt included many separate methods and operations, from which it will suffice to mention the following:

We first followed the directions of Kodyl,[1] by which the impurities of the syrup are precipitated with basic lead acetate and from the resulting filtrate, the sugars are thrown down by the addition of ammonia.

[1] Oesterreichsch-Ungarische Zeitschrift f. Zuckerindustrie u. Landwirtschaft, 20, 700, and 21, 92.

From this compound of lead and sugars, the latter are liberated by treatment with carbon dioxide or with hydrogen sulphide, and the solution thus obtained may be concentrated to a point of crystallization. Pursuing this method, we were able to obtain a small amount of sugar crystals which had the appearance of raffinose but which were accompanied by other materials of a gum-like nature which prevented their separation in the pure form.

We next employed the method proposed by Scheibler[1] which is based on the principle that strontium oxide throws down sucrose from a cold solution, but in a hot solution will precipitate both sucrose and raffinose. A twelve per cent. solution of about 300 grams of syrup received as much finely powdered strontium oxide as would be dissolved. After standing forty-eight hours, the filtrate received an additional amount of strontium oxide and was boiled for thirty minutes. An abundant precipitate resulted, which was suspended in water and decomposed by means of carbon dioxide. The filtrate from this which was supposed to contain raffinose and sucrose, was evaporated to a syrup, absorbed in dry sand, thoroughly dried and extracted with absolute methyl alcohol, but we were unable to obtain raffinose crystals from the product.

We finally made use of the following method which is a combination of the preceding ones and which proved successful.

2000 grams of syrup were freely diluted with water and treated with basic lead acetate in large excess. Neither sucrose nor raffinose form insoluble compounds under these conditions but a large amount of other material was precipitated from which the solutions were decanted, and after still farther dilution, were treated with ammonia until strongly alkaline. After standing in a warm place some forty-eight hours, a heavy precipitate had settled to the bottom of the vessels. This precipitate is supposed to consist of compounds of one molecule of raffinose or sucrose respectively, with three molecules of lead oxide. This was washed by decantation, suspended in water and treated with sodium carbonate and carbon dioxide until all of the lead had been removed. The filtrate therefrom was concentrated to a thin syrup. It was examined with the polarimeter and estimate made

[1] *Ber. d. chem. Ges.*, 18, 1409.

of the amount of sugar it contained, calculated as sucrose. Strontium oxide was added in the proportion of three molecules to one of sugar and the mixture maintained at a temperature of boiling water for three hours, during which a fine, yellowish white, granular precipitate was thrown down. This presumably consisted of strontium saccharate and raffinosate. It was noted in this and subsequent operations that it was not possible to remove all of the sugar from the solution by this process since the filtrate from these combined strontium compounds, invariably possessed a rotatory power equal to about two to four per cent. of sugar. The strontium compounds thus obtained were decomposed by treatment with carbon dioxide ; the solution filtered off and concentrated to a thick syrup. After forty-eight hours, fine crystals could be seen under the microscope, and after a week, the mass had become solid. These crystals were long and needle-like when seen under the microscope. To the naked eye they presented a silky, shimmering appearance, often gathered in bunches radiating from a common center. No crystals resembling sucrose crystals could be observed. After being thoroughly dried, these crystals showed a specific rotation of 74°. That of pure raffinose is 104° to 105°. Of pure sucrose 66.5°. These results indicated a mixture of which the greater portion was probably sucrose, although the increased specific rotation pointed to the presence of a small amount of raffinose. Attempts were made to purify this product by extracting with absolute methyl alcohol by which about half the entire mass was dissolved. This solution, on being brought to crystallization, had every appearance of pure raffinose while the insoluble residue gave a specific rotation of pure sucrose.

This process as described was repeated several times until we had obtained what appeared to be several grams of fairly pure raffinose. But while these crystals were invariably of the general superficial character peculiar to raffinose, it was found that the specific rotation of all the different preparations was very far from being that of the sugar sought, varying from 72° to 85°. The different portions were therefore combined and subjected to repeated extraction with boiling methyl alcohol. These extracts, on being brought to crystallization showed, however, that the separation of raffinose and sucrose could not be accomplished in

this way, since none of the products show a specific rotation greater than 80°.

The next step was to employ cold methyl alcohol for such fractional solutions. According to Scheibler,[1] raffinose is readily dissolved in cold methyl alcohol, while sucrose is scarcely affected. Nevertheless, upon treating our products with cold methyl alcohol, we obtained therefrom portions which, after being crystallized, possessed respectively the specific rotation of 78°, 75°, and 71.5°, showing that no progress had been made in the separation of the two sugars. Finally, all these products were once more combined, dissolved in water, and left to crystallize slowly. As soon as an appreciable amount of crystals had formed in this watery solution, they were removed, dried, and polarized. Five successive fractions thus obtained showed the following specific rotations:

I. $(\alpha)_D = 86.7°$.
II. $(\alpha)_D = 103.7°$.
III. $(\alpha)_D = 99.2°$.
IV. $(\alpha)_D = 92.0°$.
V. $(\alpha)_D = 75.0°$.

Of these portions, evidently Nos. II and III were practically pure raffinose. Nos. I and IV were united and subjected to a second fractional crystallization, from which was obtained one small portion which showed a specific rotation of over 100°.

From these results we feel justified in concluding that raffinose occurs in the juices of the American sugar beet in appreciable quantities.

Certain peculiarities observed in connection with the crystallization of these mixtures of sucrose and raffinose, seem to be worthy of special mention.

The influence of small amounts of raffinose upon the form of sucrose crystals has been much commented on and investigated. In general, it is well understood that the presence of raffinose in cane sugar tends to produce elongated, sharp-pointed abnormal crystals. But the microscopic aspect of the crystals of such mixtures has been only rarely referred to and, so far as we know, not figured.

In the course of our investigation we had frequent occasion

[1] *Ber. d. chem. Ges.*, 19, 2868.

to examine preparations of our products under the microscope, and were repeatedly surprised to observe that solutions containing apparently but a very small amount of raffinose, would completely crystallize under the microscope into forms which could scarcely be distinguished from pure raffinose.

The accompanying illustrations demonstrate this tendency far better than any mere description.

No. 1 shows the normal form of the crystals of pure sucrose seen under the microscope.

No. 2. The crystals of pure raffinose.

No. 3. The crystal form of a mixture of the two with a specific rotation of 76°.

It is to be noted that the influence of the raffinose is manifested not in the appearance of isolated raffinose crystals but in a modified and abnormal appearance of all of the crystals, which are all similar to each other but entirely distinct from those of sucrose.

This tendency on the part of raffinose to so distinctly modify the crystals of sucrose, would seem to afford a means of readily identifying the presence of small amounts of the former in mixture with sucrose.

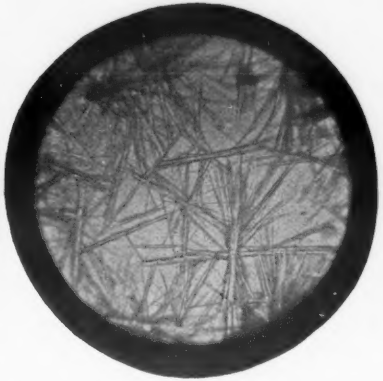
OUR PRESENT KNOWLEDGE OF ARGON, WITH A PARTIAL BIBLIOGRAPHY.

By C. LeRoy Parker.

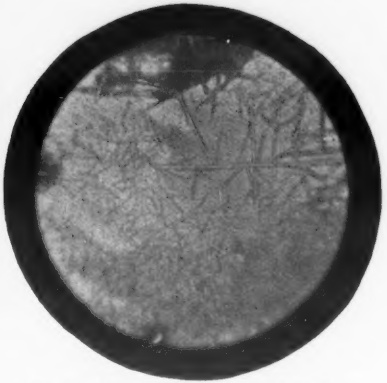
Received January 8, 1897.

SINCE the appearance of the account by Lord Rayleigh and Prof. Ramsay, of their joint discovery, there has been evident, in this country and abroad, a general air of expectation, which even the remarkable results that have been obtained have not been sufficient to remove. In fact, instead of allaying this expectancy it has rather been increased, by the accounts of researches thus far made, so that now, even more than at first, the scientific world is looking forward to the solution of the remaining problems concerning argon, with an interest, rendered particularly intense by the commonly accepted conviction that, upon the nature of the solution will depend, in a great measure, our views of certain chemical theories which we have heretofore regarded as firmly established. While the results of the inves-

No. 1. Pure Sucrose.
Specific Rotation 66.5°.



No. 2. Pure Raffinose.
Specific Rotation 103.5°.



No. 3. A Mixture of Sucrose and Raffinose.
Specific Rotation 76°.

tigations of the properties of argon fall far short of clearing up many uncertain points concerning the character of the gas, they are not without direct and important bearings on them and it is with a view of presenting and discussing the essential features of these results that this paper has been prepared.

The account of the discovery and early researches on argon, by Lord Rayleigh and Professor Ramsay, has been given such wide circulation and these have now become matters of such familiar knowledge to chemists that I will take up the time of the Society, in connection with them, only so far as is necessary to sum up their results and consider them briefly in connection with those subsequently obtained.

In order to successfully study the character of argon it was necessary, first of all, to obtain it in considerable quantities in a pure state. The first method, sometimes and very appropriately called the Cavendish method, since it is the one by means of which Cavendish isolated and measured an impurity in atmospheric nitrogen, consisted in passing electric sparks through a mixture of air and oxygen—mixed in about equal quantities—confined in a eudiometer over dilute alkali. When all of the nitrogen had combined with the oxygen and been absorbed by the alkali, the excess of oxygen was absorbed by alkaline pyrogallate, leaving the required gas free. A second method, by means of which argon could be obtained more satisfactorily and in larger quantities, consisted in passing pure dry air over red hot copper, which removed the oxygen, and then over heated magnesium, which removed the nitrogen, the inert gas being left. This process, which is here merely outlined, required a circulation of not far from two days through the system of tubes containing the absorbents before the argon could be obtained pure. The argon used in many of the most recent investigations was obtained by keeping up an electric arc in a mixture of air and oxygen for about two days, removing the nitrogen and oxygen as already described. Other methods for obtaining argon have been suggested, but their utility has yet to be demonstrated.

The proportions in which argon exists in the atmosphere was ascertained by the experiments which led to the discovery of the gas, to be about $\frac{1}{125}$ by volume and $\frac{1}{120}$ by weight. The most

recent investigations on this point are those of Th. Schloesing,[88] who has found that the proportion of argon in atmospheric nitrogen is 0.0119, a result which agrees to a remarkable degree with those obtained by Rayleigh and Leduc. Schloesing has further shown[88] that in the case of argon, as with oxygen and nitrogen, its proportion in the atmosphere varies to a degree scarcely perceptible on analysis. Kellas, who has made researches along somewhat the same line as those of Schloesing, has found[60] that argon exists in a greater proportion in respired air than in normal air. In the researches on the occurrence of argon other sources than the atmosphere have been discovered. It has been found to be given off in small quantities, in connection with other gases, when clevite, samarskite, euxenite, and a few other minerals are treated with acids or heated *in vacuo*,[33] but as yet the condition in which argon exists in these minerals has not been determined.[68] A still more interesting source of argon is that of meteoric iron, which was found in Augusta County, Virginia. The specimen was analyzed by Prof. Ramsay and found to contain the inert gas.[35] Argon has been discovered in the waters of a number of mineral springs. Bouchard has found it in certain springs in the Pyrenees,[49] Kayser in the springs of Wildbad, in the Black Forest,[48] Rayleigh in the Bath Springs,[77] and Ch. Mouren has found that it constitutes a part of the gases which escape abundantly in bubbles from the spring of Maizières[64] (Côte d'Or). Bedson and Shaw have found argon in the gases enclosed in rock salt,[41] and Th. Schloesing has discovered it to be a constituent of fire damp and of the gas of Rochbelle.[83] Argon has been sought for without success in animal and vegetable substances[23] by Geo. MacDonald and A. M. Kellas, but Schloesing and Richard, as a result of an investigation, which shows something of the extent to which researches on the occurrence of argon have been carried, have found that it forms a part of the gases of the natatory bladder of fishes and physaliæ.[74]

Concerning the true character of argon there have been many and varied opinions advanced, but none so widely accepted as the one originally advanced by the discoverers of the gas, which is that it is an element and monatomic.[5] It has been suggested that argon might be an oxide of nitrogen, a view speedily dis-

carded when the methods of isolating argon became better understood. Another view advanced by Dewar[3] and others is that argon might be an allotropic form of nitrogen bearing the same relation to that element that ozone does to oxygen. This would explain the concurrent existence of argon and nitrogen, and the fact that many of the lines of their spectra are near to each other. It would also explain the inactivity of argon and would allow it a proper place in the periodic system. Against this view are the facts that in decomposing compounds of argon no nitrogen is detected and that in no way has any one succeeded in obtaining nitrogen from argon or argon from pure nitrogen, and that, if we adopt N_3 as the formula of argon its density would not at all conform to the density found for argon. Further evidence against this theory is found in the results of researches by Peratoner and Oddo,[55] who, observing that the molecular weight of argon approximates that of a triatomic polymeride of nitrogen, made a number of experiments on a gas obtained by the decomposition of aziomide, but could find no trace of argon.

The view suggested by Crookes in his paper on the spectra of argon,[6] that the discoverers of argon may have added "two members to the family of elements" has been somewhat extensively adopted. This view exhibits the least incompatibility with our present theories of chemistry and, if shown to be the true one, will remove the grave suspicions which since the discovery of argon have rested on the periodic classification of the elements. The fact of the duality and simultaneous appearance of the spectra of argon, which, as Friedländer has pointed out,[55] has been regarded as evidence of the compound nature of the gas, cannot rightfully be so regarded since the same phenomena have been observed by W. N. Hartley in connection with nitrogen, which is of undoubted elementary character.[56] The observation of three different spectra of argon, by Eder and Valentia,[71] appears to have a very important bearing on the theory suggested by Crookes and to deserve careful consideration in forming our opinions concerning the elementary or compound character of argon.

Whatever other light spectroscopic investigations may throw upon this question, this much is certain, as Hartley has pointed

out,[86] that since no compound gaseous substance known can withstand the temperature of the electric spark, without exhibiting the spectra of its elements, and since the spectra of argon are not those of any other known substance it follows that, if the gas is a compound, all of its constituent elements have been hitherto unknown.

The most commonly accepted view concerning argon, *viz.*, that it is an element, is based chiefly upon the evidence of its being monatomic. As pointed out in their original paper,[5] Lord Rayleigh and Prof. Ramsay found the ratio of the specific heats of argon to approximate 1.67, which is the theoretical ratio of the two specific heats of a monatomic gas.

In the absence of contradictory evidence, this fact would have been considered satisfactory proof of the monatomicity of the argon molecule and the consequent elementary character of the gas, but the density of argon, having been found to be approximately twenty, the atomic weight would, if the molecule contains but one atom, be forty, in which case there would be no proper place for it in the periodic system. To accept one as the atomicity of argon means the overthrow of the present classification of the elements. On the other hand, to assume that argon has an atomicity other than one, in which case it finds a proper place in Mendeléeff's system, is in direct opposition to the kinetic theory, which has not hitherto been called into question.

Still other theories have been advanced to explain the nature of argon. Nasini has suggested that it might be a diatomic gas. but with its atoms so nearly spherical as to make it resemble a monatomic gas in certain respects.[40] This view is thought to afford the best explanation of the peculiar character of argon by a great number of the chemists who doubt its monatomicity. Another view is that argon contains both monatomic and diatomic molecules. This view, which was referred to by Prof. Ramsay in his lecture given before the Oxford Junior Scientific Club on a recent date,[78] is regarded by him, as it is by chemists generally, as being improbable in the extreme.

In the investigation of the physical properties of the new gas the ground has been so thoroughly covered that we can hope for no extensive advance in this direction.

The density of argon, which it has thus far been found im-

possible to completely reconcile with its other properties, was found by Lord Rayleigh to be 19.94.[67] The refractivity and viscosity were found by the same physicist to be respectively 0.961 and 120, air being the standard.[53]

As regards the spectra of argon, the early and accurate knowledge of which has been of incalculable value to the investigators of the gas, Mr. Crookes[6] noticed that at the end of the capillary tube containing the argon, near the positive pole, there appeared a reddish, and at the end near the negative pole, a bluish glow, two spectra being produced, twenty-six lines of which appeared to be common.

In comparing the spectra of argon with the sharp line spectrum of nitrogen Mr. Crookes says: "The sharp line spectrum of nitrogen is not nearly so striking in brilliancy, number or sharpness of lines as those of argon, and the most careful scrutiny fails to show any connection between the spectra. I can detect no lines in common." Between the band spectrum of nitrogen and the spectra of argon Mr. Crookes observed two or three close approximations of lines, but no positive coincidences.

Eder and Valenta have observed that in addition to the red and blue spectra there is a third spectrum produced when very large condensers are used with a Ruhmkorff's coil and powerful currents employed in the primary circuit.[71] This third spectrum is distinguished from the other spectra in that many of the lines appear more distinct while others are less so, and by the appearance of entirely different lines as well.

In connection with the red and blue color, which Crookes has observed, it is interesting to note that, during the action of the silent electric discharge in a mixture of benzene vapor and argon, Berthelot observed an intense greenish fluorescence, and that this gave a spectrum showing lines and bands in the yellow, green, and violet, similar to those observed in the spectrum of the aurora borealis.[28] While none of the lines coincided exactly with the principal line of the aurora borealis, 557, the argon line 555.7, is very near the latter and Berthelot is convinced by his comparative study of the two spectra, that there is some relation between the presence of argon in the atmosphere and the production of the aurora borealis.

At the time of the discovery of argon no chemical properties

of the gas, other than its extreme inertness, had been discovered, hence the name argon, from the Greek prefix ἀ- privative meaning without and ἔργον, work. Although subsequent researches have shown the term to be, in a strictly literal sense, a misnomer, it is not to be overlooked that the name argon was only given after repeated attempts to induce chemical combination of the gas with other elements had been made.

The following is a list of the more important experiments made at that time and subsequently, with a view of studying the chemical properties of argon. It was mixed successively with oxygen, hydrogen, and with moist and dry chlorine and subjected to the action of the silent electric discharge without undergoing change. It was brought in contact with sulphur and phosphorus at a red heat and no change took place. Tellurium was distilled in the gas, as were sodium and potassium, without losing their luster. It was not absorbed by red hot caustic soda nor soda lime. It passed unaffected over red hot potassium nitrate and sodium peroxide. Persulphide of sodium and calcium were without action on it at a red heat. Platinum black did not absorb it nor did platinum sponge. Wet oxidizing and chlorinating agents, as potassium permanganate, aqua regia, bromine water, bromine and alkali, and hydrochloric acid were entirely without action upon the gas. It resisted the action of nascent silicon and boron, as proven by contact with a mixture of sodium and silica, and one of sodium and boric anhydride. It was subjected to the influence of the electric spark in contact with fluorine, boron, titanium, lithium, and uranium without inducing chemical action.

An apparent combination of argon and carbon was observed by Prof. Ramsay by making an arc between two rods of purified carbon in an atmosphere of argon.[43] Further investigation along the same line,[76] however, here led to the conclusion that argon does not combine with carbon even at the temperature of the electric arc and that the expansion which led to the inference that a chemical union had taken place was due to the carbon dioxide gas occluded on the surface of the carbon not being entirely removed, before the rods were introduced into the argon receiver. As further evidence bearing upon the possible union of argon and carbon, a mixture of carbon tetrachloride and argon was exposed for several hours to a silent electric dis-

charge. The argon did not enter into combination but was recovered without loss.

Other attempts to induce argon to enter into combination have been singularly successful. Berthelot, by means of the silent electric discharge, has effected the union of argon with benzene,[20] carbon disulphide,[36] and apparently with mercury. Berthelot describes the product formed by the union of argon with the elements of benzene, the first compound of argon produced in the laboratory, as consisting of "yellow resinous matter which, under the action of heat, decomposes, forming volatile products and leaving a bulky carbonaceous residue."

Troost and Ouvard appear to have been able to effect the combination of argon with the vapor of magnesium by means of a powerful electric discharge.[50] Argon contained in a tube, furnished with magnesium wires connected with a Ruhmkorff's coil, was found to gradually diminish in volume under the influence of the discharge and finally to disappear, seemingly becoming united with the vapor of the magnesium. Under the same conditions platinum appeared to volatilize and combine with the argon in the same manner as the magnesium.

P. Villard has found that upon being compressed to 150 atmospheres, in presence of water, argon combines with the water to form a crystalline and dissociable hydrate, which is analogous to the hydrates of gases already known.[54] Almost as remarkable as the discovery itself is the failure on the part of chemists to detect argon previous to 1894. Cavendish isolated the gas, apparently obtained it in a pure state, and the account of his research has been in the hands of chemists for a hundred years. Simply because Cavendish inferred the relative freedom from impurities of his "phlogisticated air," from the smallness of the residuum he obtained, chemists were willing to leave the critical investigation of this residuum to the future until its explanation became necessary in clearing up other difficulties. It would be hard to find an example of a fallacy, arising from undue devotion to authority, more instructive than that of our mistaken views regarding the composition of the atmosphere previous to Lord Rayleigh's and Prof. Ramsay's brilliant discovery.

It is further interesting, in connection with the long delay in

detecting argon, to note the researches of Mallet, who, in 1870, published an account of an industrial method for preparing oxygen,[1] in which he unknowingly describes what could not fail to be the production of, if not pure, at least highly accumulated argon in connection with oxygen. Mallet's method consists in repeatedly pumping air into water, under high pressure, liberating the absorbed gases and again pumping them into water, repeating the process until the oxygen is sufficiently freed from other gases, for the use to which it is to be applied.

The isolation of the argon from the nitrogen would result, as Brauner has pointed out,[17] from the superior solubility of the former gas, the solubility of argon in water being to that of nitrogen in the ratio of 2.5 to 1. Repeating the process eight times produces a gas which, according to Mallet, consists of 97.3 per cent. of oxygen and 2.7 per cent. of nitrogen. That this so-called nitrogen is really nearly pure argon there can be little doubt; in fact, that the action of the process is, as here described, is proven by the fact that the curve representing graphically the decrease in the percentage of nitrogen after each operation shows that after the first few repetitions of the process the absorption coefficient of the so-called nitrogen which is gradually becoming richer in argon, approaches the coefficient of absorption of oxygen which is approximately the same as that of argon.

The failure to detect argon previous to 1894 is the more remarkable from the fact that the records of the progress of chemistry abound with accounts of atmospheric research. As Brunner has said "L'analyse chemique de l'atmosphère a été de tout temps une des parties de la chimie qui est attirê le plus l'attention des savants." A single periodical, the *Chemical News*, *1860-1896*, describes about 200 investigations on air, and yet, notwithstanding the abundance of such researches, a careful survey of the literature on the subject since the time of Cavendish's classic experiments to those of Rayleigh fails to reveal even so much as a surmise that the air contained any gas which had not been isolated and studied.

It is not the author's intention to infer from this that the discovery of a gas, of the character of argon, had never been pre-

[1] *Ding. poly. J.*, 199, 112; *J. für Gasbereitung*, *1870*, 538.

dicted, but merely to show that no such predictions has been made as a result of the study of the atmosphere.

There are two very remarkable instances of the anticipation of the discovery of argon. The first was that of Lieut. Col. Sedgwick, in 1890, and the second that of Boisbaudran shortly before the discovery of argon was announced.

Sedgwick, as a result of his study of the forms and relations of atoms, reached the conclusion that there must be an inactive element of the atomic weight commonly assigned to argon. He conceives atoms to be spheres with one or more flat places, the number of which correspond to the valence of the element. Sedgwick, on page 60 of his book "Force as an Entity," published in 1890, points out that an element whose atoms are perfect spheres, would be inactive and have an atomic weight of 20.

In his remarks on atomic weights[1] Boisbaudran gave a classification of the elements which led him to assume the existence of an unknown family of elements of atomic weights 20.0945, 36.49 ± 0.08, 84.01 ± 0.02, and 132.71 ± 0.85. These elements, according to Boisbaudran, should be non-metallic, of even atomicity, the first two abundant in nature, and the member having the atomic weight 20.0945, which he now identifies with argon, should be more volatile than oxygen.

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A RAPID METHOD FOR THE DETERMINATION OF SILICON IN SILICO-SPIEGEL AND FERRO-SILICON.

By C. B. Murray and G. P. Maury.

Received January 27, 1897.

IN 1894 Furnace "A" at the Edgar Thomson Steel Works made the first silico-spiegel ever manufactured in this country. A determination of silicon and manganese was required in each cast, the silicon especially, as soon as possible.

The "aqua regia" method was the one tried. Various strengths of acid were used, but it was found almost impossible to get the metal into solution, even after passing the crushed "shot" through bolting-cloth. As high as 400 cc. aqua regia was used on one-half gram, the aqua regia being four parts nitric acid and three parts hydrochloric acid.

The fusion method, as recommended by Williams,[1] was also tried, but we were never able to make a determination in less than six to eight hours. The furnace made only a short run on silico-spiegel and for the time the matter was dropped. Last year we again made some silico-spiegel and were successful in finding a method for determining the silicon in a rapid and accurate manner and give the method in detail below.

Preparation of the Sample.—For the success of the method it is essential that the sample should be in a very fine state of subdivision. Grind in an agate or crush in a diamond mortar so that the sample will pass through a sieve made of bolting-cloth.

[1] *Trans. Am. Inst. Min. Eng.*, 17, 542.

Operation.—One-half gram of the sample is placed in a porcelain or platinum dish; fifty cc. water, ten cc. hydrochloric acid (1.20 sp. gr.) and twelve cc. sulphuric acid (one part sulphuric acid, 1.84 sp. gr., to three parts water) are poured on it; heat until copious fumes of sulphuric acid are given off. Allow the dish to cool, so that there will be no spattering when taking up with acid. When cool, add about ten cc. hydrochloric acid, heat to soften the sulphate of iron, add about seventy-five cc. water, and bring to a boil. Discontinue the heating and note whether there is any effervescence when boiling ceases. If there is, the liquid must be evaporated until copious fumes of sulphuric acid are given off again, then taken up as before directed. Filter at once, wash thoroughly with hydrochloric acid (1 : 1) and hot water, ignite in a platinum crucible, and weigh. Add a few drops sulphuric acid and enough hydrofluoric acid to dissolve the silica. Evaporate to dryness, heat to decompose the sulphates, cool, and weigh. The difference in the two weights is silica, which can be calculated to silicon. The whole operation can be accomplished in thirty minutes.

The following are some results, both by our method and the fusion method:

No.	Our method.	Fusion method.
1	12.08	12.01
2	12.37	12.25
3	12.09	12.08
4	13.46	13.40
5	9.05	9.03

A METHOD FOR THE COMPLETE ANALYSIS OF IRON ORES, WITH NOTES ON SÄRNSTRÖM'S METHOD OF DETERMINING MANGANESE.

BY GEORGE AUCHY.

Received January 25, 1897.

SÄRNSTRÖM'S method of determining manganese in iron ores, as described by Messrs. Mixer and DuBois, is to precipitate the iron in dilute hot solution by sodium carbonate, care being taken to add no more of this reagent than just enough to effect the precipitation of the iron; then titrating (without filtering from the precipitated ferric oxide) with standard permanganate. The writer, in experimenting with Volhard's method,

and with Stone's modification of Volhard's method, had found that in working these methods it was necessary to add the zinc oxide in considerable excess of the amount necessary to completely precipitate the iron, for the reason that titration of the manganese in imperfectly neutralized solution gives too high results. But in Särnström's method we have, apparently, titration in incompletely neutralized solution without any tendency to high results as a consequence, as is shown by the accuracy in Messrs. Mixer and DuBois' work. It was thought by the writer that this apparent anomaly could perhaps be explained by the assumption that in Särnström's method manganese is carried down by the iron precipitate, as happens in Volhard's method, if certain precautions be not observed, and that this error compensates for the error of high results due to titration in incompletely neutralized solution. But the uniform excellence of the results given by Messrs. Mixer and DuBois operate against this view, and the following experiments made by the writer also seem to show that Särnström's method is free from these sources of error :

Manganese present. Per cent.	Manganese found. Per cent.	Number of cc. permanganate required, theoretical.	Number of cc. permanganate required, actual.
0.60	0.60	2	2.0
0.60	0.60	2	2.0
0.60	0.60	2	2.0
0.60	0.60	2	2.0
1.80	1.68	6	5.6
1.80	1.80	6	6.0
3.60	3.54	12	11.8
3.60	3.60	12	12.0
7.20	6.96	24	23.2
1.80	1.80	6	6.0
1.80	1.80	6	6.0
1.20	1.20	4	4.0
1.20	1.14	4	3.8
1.80	1.74	6	5.8
1.80	1.74	6	5.8
0.60	0.60	2	2.0
2.40	2.37	8	7.9
3.00	2.97	10	9.9
3.60	3.54	12	11.8
4.80	4.74	16	15.8
4.80	4.74	16	15.8

Manganese present. Per cent.	Manganese found. Per cent.	Number of cc. permanganate required, theoretical.	Number of cc. permanganate required, actual.
6.00	5.94	20	19.8
1.80	1.81	6	6.05
1.20	1.19	4	3.95
2.40	2.37	8	7.9
3.60	3.66	12	12.2
4.80	4.84	16	16.15
6.00	5.97	20	19.9
7.20	7.14	24	23.8

It would seem from these results that there is a tendency to slightly low results; but that this is not due to manganese carried down with the iron precipitate seems shown by the fact that the same tendency exists when no iron is present. The following tests were made with manganese solutions free from iron, having exactly the same amounts of free acid present as in the previous experiments, and also using exactly the same amounts of sodium carbonate for neutralization.

Manganese present. Per cent.	Manganese found. Per cent.
0.60	0.60
0.60	0.60
0.60	0.57
1.20	1.20
2.40	2.37
3.60	3.54

There seems to be an entire absence of the tendency to high results existing in Volhard's method when titration is performed in incompletely neutralized solution. But further experiments led the writer to question whether, after all, he was right in his assumption that the titration in Särnström's method takes place in incompletely neutralized solution; and the experiments following seem to indicate that the explanation of the mystery lies in the fact that in Särnström's method either the ferric oxide by its presence, in some way, prevents high results when solutions are incompletely neutralized, or the ferric oxide by its presence, in some way, prevents the precipitation of the manganese dioxide by titration, except the solution be thoroughly neutralized when titrated, the permanganate simply coloring the solution, and no manganese dioxide precipitating until more sodium carbonate is added. If the solution—incom-

pletely neutralized, but sufficiently so to precipitate the iron—be filtered from the precipitated ferric oxide before titration, the manganese in that case is not held up (if the solution be not too acid) but precipitates immediately upon the addition of the permanganate, and the result then becomes too high, as in Volhard's method, under similar conditions of neutralization.

Manganese present.	Manganese found; filtered from the ferric oxide before titration.	Manganese found; filtered from the ferric oxide, but more sodium carbonate added before titration.
Per cent.	Per cent.	Per cent.
3.60	3.66	3.60
3.60	3.63	3.60
3.60	3.66	....
3.60	3.75	....
3.60	3.75	....

It should be noted that when in the performance of the method by the regular way, the neutralization happens to be imperfect, and the permanganate therefore fails to throw down the manganese dioxide, and more sodium carbonate is consequently added, the result is apt to be too high if *much* more sodium carbonate is required, as appears from the following:

Manganese present. Per cent.	Manganese found. Per cent.
2.40	2.43
0.60	0.67
0.60	0.63

If little more sodium carbonate is required the result is not affected.

Manganese present. Per cent.	Manganese found. Per cent.
0.60	0.60
0.60	0.60
1.80	1.80
2.40	2.37
4.80	4.74
6.00	5.94
1.80	1.81
1.20	1.23

At all times an excess of sodium carbonate must of course be guarded against, but the exact point of neutralization can invariably and easily be obtained by performing the process as follows: Add seven grams of ammonium chloride; make the bulk of the solution 400 or 500 cc., add sodium carbonate *in the*

cold to a slight but permanent turbidity; toward the last the sodium carbonate solution is added drop by drop from a burette; when a slight turbidity appears, which, if anything, increases by standing a minute but which shows no sign of a distinct precipitate, the reaction is complete (Herschel and Schwartzenberg). Bring to a boil with frequent stirring, which precipitates the iron completely; then add one cc. more of sodium carbonate solution (one pound of crystallized salt to one liter of water), and titrate with permanganate. By performing the process in this way accurate results are invariably obtained. The ammonium chloride present makes the danger of manganese precipitating through an excess of sodium carbonate very remote, even if much more carbonate be added than directed. One-tenth cc. of permanganate (when the strength is 0.0056) should be deducted from the reading of the burette, as a performance in blank shows that that much permanganate is required to give a distinct color to a solution of that bulk.

The phenomenon noted in the examination of Volhard's method, that titration in nitric acid solution requires a deduction to be made in the result of 0.02 per cent.[1] also occurs in Särnström's method, as was shown by two experiments.

The Särnström method may be successfully used in steel analysis provided—as Messrs. Mixer and DuBois have said—that organic matter be first destroyed. But Stone's modification of Volhard's method is preferable, since in that method the organic matter does not interfere, being carried down with the ferric oxide and filtered off, and hence the time consumed in destroying the organic matter may be saved.

It is the writer's experience that the color method is, all things considered, as good as any for common use. But it is perhaps worth remarking that in the color method a standard *solution* is preferable to standard drillings, the time and labor of weighing out and dissolving the standard drillings for every analysis being thereby saved. In making up the standard manganese

[1] It is better to say that a deduction of 0.2 cc. permanganate (strength 0.0056) is required. With the weight of sample taken for analysis by Volhard's method this amounts to 0.02 per cent., as stated. But in Särnström's method only about one-third of this weight can be taken, and the deduction therefore would be 0.06 per cent. instead of 0.02 per cent. It would therefore have been better if in the article on Volhard's method the writer had directed a deduction of 0.2 cc. permanganate instead of a deduction of 0.02 per cent. in the result.

solution, the amount of nitric acid used for solution of the standard steel should, of course, be such that 100 cc. of the standard solution will contain as much acid as is used for solution of the steel to be tested. Ten cc. of the standard solution is in each case used, three cc. dilute nitric acid added, boiled with lead peroxide, etc.

A METHOD OF ANALYZING IRON ORE.

In making a complete analysis of iron ore it seemed an obvious application of Särnström's method to separate manganese, lime, and magnesia from iron by precipitating the iron as in that method, and filtering before titrating with permanganate. The writer had no access to Särnström's original article, but from the tone of the description of it given by Messrs. Mixer and DuBois, inferred that no such application is made by Särnström. In Crookes' Select Methods iron is separated from manganese in this way; also manganese from zinc; but there is no mention of lime and magnesia in this connection. Fresenius (old edition) gives a method by Herschel and Schwarzenberg for separating "iron sesquioxide from nickel, cobalt, zinc, manganese, and other strong bases" by neutralizing with ammonium carbonate in the cold in presence of much ammonium chloride, till the liquid loses its transparency, and does not clear up after a moment's standing, but, if anything, shows an increased cloudiness, without showing the least trace of a distinct precipitate; then bringing to a boil and boiling to expulsion of the carbon dioxide, and filtering from the completely precipitated basic iron oxide. But the writer was not sure that lime and magnesia were included in the term "strong bases;" and moreover, had much doubt as to the efficacy of the separation in the case of alumina. Experiments were therefore made on his own account, which showed that in carrying out the process, as already described in the first section of this article, namely, neutralization with sodium carbonate in the cold to slight but permanent turbidity, but with no trace of a distinct precipitate showing, then bringing to a boil, adding afterwards one cc. more of sodium carbonate solution, and filtering from the iron oxide, it occurs:

1. That in the absence of alumina all the zinc, manganese, and lime are found in the filtrate from the ferric oxide, but not

all the magnesia, which latter requires therefore a repetition of the operation for a complete separation from the iron.

2. That if seven grams of ammonium chloride be added to the solution before neutralization with sodium carbonate and precipitation of the iron, the separation of the magnesia, as well as that of the manganese, zinc, and lime, is, in that case, thorough and complete in one precipitation.

3. That if alumina be present, however (seven grams of ammonium chloride being also present), the alumina not only is not itself completely separated from the iron in one precipitation, but the small amount of alumina precipitating with the iron also carries with it a small amount of the magnesia or lime, or both (the test was made by adding phosphate and ammonium chloride to the concentrated filtrate from a basic acetate precipitation), and therefore two, and very often three precipitations are necessary to get the ferric oxide completely free from alumina, lime, and magnesia.[1]

4. That the presence of alumina in solution with the manganese, after filtration from the ferric oxide, interferes with the titration with permanganate, as the addition of the small quantity of sodium carbonate necessary to a thorough neutralization before titration, partially precipitates the alumina, and this keeps the manganese dioxide precipitate from balling together, thereby preventing any observation of the color of the liquid; while if enough sodium carbonate be added to completely precipitate the alumina—although the titration can then be successfully performed—the result will be too low, the alumina apparently carrying down some of the manganese.

5. That if the alumina be precipitated by ammonia in slight excess, boiling off the excess, no manganese is carried down, and the manganese in the filtrate from the alumina may be conveniently and accurately determined by titration with permanganate.

With these facts ascertained, the scheme for analysis of iron ores would obviously be as follows:

[1] It should be noted, however, that the experiments on this point were made with a solution containing also titanic acid, equivalent to one per cent.; so that it is probably the titanic acid which carries down the alumina. But as titanic acid in small amount is so frequently a constituent of iron ores, it was not thought necessary to investigate this point.

Take one-half gram of the ore for analysis. Dissolve and separate silica as usual. To the filtrate from the silica add two hornspoonsful (about seven grams) of ammonium chloride, and dilute to 275 cc. (or 300 cc. in rich ores). Add sodium carbonate solution (or the main part of the neutralization may conveniently be made with the solid carbonate[1]) from a burette, toward the last, after the solution turns from yellow to red in color, drop by drop, till the appearance of a faint cloudiness which persists on standing a minute, or even increases, without, however, showing any trace of a distinct precipitate.[2] Then bring to a boil with frequent stirring, the ferric oxide beginning to precipitate as soon as the heat is applied. Boil a few minutes. Add five drops more of sodium carbonate from the burette (about three-tenths cc., sodium carbonate solution of strength one pound crystallized salt to a liter of water) and stir. Allow to stand until the ferric oxide precipitate has completely settled. Filter and wash (not by decantation) with hot water.[3] The ferric oxide precipitate contains besides the titanic acid and phosphoric acid, also a small portion of the alumina, lime, and magnesia. Dissolve on the filter in hot hydrochloric acid, add the solution of the alumina later obtained, and precipitate with ammonia. Filter and weigh, and estimate alumina by difference. The filtrate from this precipitate—containing the small amount of magnesia or lime, or both, coming down with the iron in the first precipitation—is added to the main lime and magnesia solution after the latter has been freed from the manganese, as described later.

The filtrate from the first ferric oxide precipitate containing all the manganese, and all but a small part of the lime, alumina, and magnesia (and 0.01 or 0.02 per cent. of phosphoric acid if the phosphorus in the ore be extremely high, afterwards precipitated with the alumina) is brought to a boil and boiled a minute to expel traces of carbon dioxide (a very necessary pre-

[1] Ammonium carbonate, if free from organic matter, doubtless answers just as well, or probably better, as ammonium salts are desired in the solution, while sodium salts are of no use. But the writer prefers sodium carbonate on account of cheapness, and on account of being free from organic compounds, which interfere with the subsequent titration with permanganate.

[2] In observing the liquid, it is well to do so both by holding it between the light and the operator, and by reflected light. The cloudiness is best recognized, however, by working by reflected light.

[3] A nine cm. filter paper is hardly large enough, and either a size or two larger should be used, or else two nine cm. filters. After the first two washings the precipitate should be stirred up by the jet.

caution), ammonia added in slight excess, and the excess boiled off. The precipitated alumina, free from manganese, but carrying a little magnesia when much is present, is allowed to settle, filtered (by siphon preferably), and washed with hot water. Dissolve in hydrochloric acid and add to the ferric oxide solution. The filtrate from the alumina is brought to a boil and titrated with standard permanganate. Deduct from the reading of the burette the number of cc. of the permanganate taken up by the organic matter of the ammonium chloride used—previously ascertained by a trial in blank—and calculate the percentage of manganese. Add a small crystal or two of oxalic acid, and some hydrochloric acid to get the precipitated manganese again into solution (the manganese dioxide cannot be filtered off because it carries magnesia). Destroy the excess of oxalic acid by titrating with permanganate solution. Evaporate down and precipitate and filter the manganese (as sulphide) as directed in Blair's Chemical Analysis of Iron, and finish as usual—but determining the lime by titration with permanganate.

This method of analysis has the advantage over the basic acetate in that the precipitation of the iron takes place in small, instead of large, bulk of solution, with a consequent saving of time in evaporation ; the separation from the manganese by the former process, moreover, being thorough and complete, while by the basic acetate, two basic acetate precipitations are necessary for a thoroughly accurate separation. If two basic acetate precipitations be made, the proposed method is very much quicker, but is also quicker if only one basic acetate be made. In the basic acetate method, no separate precipitation and filtration of the alumina is involved, but this precipitation and filtration requires considerably less time than is required to evaporate down the filtrate from the basic acetate precipitation to a workable bulk. Another advantage in the proposed method is in the determination of manganese by titration instead of by the rather tedious and troublesome gravimetric process. Still another is in the fact that the iron precipitate by the proposed method is one that shows no tendency to run through the filter, settles more rapidly, and is washed with much more ease than the basic acetate precipitate ; moreover, this precipitation is simpler and more likely to be successfully performed by a beginner.

Following are some manganese results obtained in this way :

No.	Manganese present. Per cent.	Manganese found. Per cent.
1	3.60	3.60
2	3.60	3.60
3	3.60	3.60
4	3.60	3.60
5	3.60	3.60
6	3.60	3.54
7	3.60	3.60
8	3.60	3.36

The last result of the series is a poor one, some of the manganese evidently having precipitated with the alumina. This seemed a very singular circumstance in view of the fact that it is laid down by authorities that manganese is completely separated from alumina by precipitation of the latter with ammonia, and boiling off the excess ; all the writer's other experiments also went to prove the same thing. It was thought that perhaps the manganese had come down with the iron precipitate instead of with the alumina, but a careful examination of the iron precipitate showed no trace of manganese. Finally it occurred to the writer that a little carbon dioxide might have been in solution at the time of the alumina precipitation—it was remembered that the ammonia had been added before the liquid had been brought to a boil. To see whether in such an event manganese would precipitate a test was made by taking standard manganese solution, adding to it the amount of hydrochloric acid used in ore analysis, nearly neutralizing with sodium carbonate as usual, heating, but not to boiling, then adding the ammonia in slight excess, and bringing to a boil. Manganic oxide was seen to precipitate ; hence the necessity for the precaution already spoken of, of boiling the liquid before precipitating the alumina with ammonia.

That titration of the manganese solution, obtained in this way, by permanganate succeeds when no carbon dioxide is present, is shown by the following tests :

No.	Manganese present. Per cent.	Manganese found. Per cent.
1	3.00	3.03
2	1.20	1.19
3	1.80	1.80
4	2.40	2.40

If in the ore to be analyzed, zinc, nickel, and cobalt are to be tested for, the scheme of analysis just described must be modified as follows :

In the filtrate from the ferric oxide precipitate the alumina, manganese, nickel, cobalt, and zinc with ammonium sulphide, filter, dissolve in hydrochloric acid, filter from sulphides of nickel and cobalt remaining undissolved, and make a basic acetate separation in small bulk, and separate the zinc, nickel, cobalt, and manganese as usual, except that manganese is determined by titration, in solution made neutral by adding ammonia and boiling off the excess, instead of being determined as phosphate.

Another scheme of analysis by which alumina is directly estimated and iron is determined volumetrically in the same sample is to make *two* ferric oxide precipitations by neutralization with sodium carbonate as described, uniting the filtrates, precipitating, filtering, and weighing the alumina (if zinc, nickel, and cobalt are not to be tested for), which may afterwards be tested for iron ; titrating the filtrate from the alumina for manganese, etc. ; the ferric oxide precipitate being dissolved, reduced, and titrated for iron, no separate iron determination being made. But if this procedure be followed it is absolutely necessary to make a third ferric oxide precipitation as described, by way of precaution ; and if much titanic acid be present the writer is doubtful if even three precipitations will always free the ferric oxide entirely from alumina (and from magnesia or lime, or both, which comes down as long as the alumina does), although he has not, as yet, made any experiments on this point. In the table of manganese results, numbers 2 to 5, inclusive, were obtained in this way.

For the experiments on these methods a solution was used containing iron equivalent to forty per cent. ; alumina equivalent to ten per cent. ; manganese 3.60 per cent. ; lime fifteen per cent. ; magnesia fifteen per cent. ; phosphoric acid two per cent. ; titanic acid one per cent. These experiments need not be given in detail.

Further experimenting—which the writer at present has not the opportunity to perform—is intended. For instance, in the first method of separation described—precipitation of the iron by

neutralization with sodium carbonate, followed by a second precipitation of the iron (and alumina) by ammonia—when zinc, nickel, and cobalt are present, experiment might perhaps prove it feasible to completely precipitate these metals as sulphides by hydrogen sulphide in the filtrate from the first ferric oxide precipitate; afterwards precipitating the alumina by ammonia and determining the manganese by titration as directed in the scheme for analysis when no zinc, nickel, and cobalt are present. Nickel and cobalt could undoubtedly be completely precipitated in this way, and the writer has hopes that the zinc, also, would be completely thrown down from the dilute, nearly neutral solution. At least by the aid of sodium dithionate, the zinc would be completely precipitated.[1] In that case, this method of separation would be simpler and more convenient than the one suggested. In the method suggested it would perhaps be better to separate the zinc, nickel, and cobalt from the alumina by ammonia and ammonium chloride instead of by a basic acetate precipitation.

No experiments have been made by the writer regarding the accuracy of the separation of the magnesia from the iron and alumina by these two precipitations described in the first method (precipitation by neutralization with sodium carbonate, followed by precipitation by ammonia). It was not thought necessary to experiment on this point, because authorities unite in considering the separation of iron and alumina from lime and magnesia by a precipitation of the former by ammonia to be sufficiently accurate—one precipitation being considered by Blair sufficient to separate all the lime and magnesia from the iron and alumina; in this method two are used—only one by ammonia, but the first precipitation, by neutralization, in all probability separates nearly as large a proportion of the magnesia as a precipitation by ammonia would do, and quite as large a proportion of it as a basic acetate precipitation would effect. But it is considered that the basic acetate separation of magnesia from iron and alumina is rather better than the separation by ammonia; and if desired, the second ferric oxide precipitation of the method suggested may of course be made by basic acetate. But in this event it is the writer's opinion that the precipitation may be made in much less

[1] J. Ribon: *Bull. Soc. Chim.*, 50, 518.

bulk (say 400 cc.) to separate the iron and alumina from the trifling amount of magnesia remaining from the first separation by neutralization, than is ordinarily required.

A quicker way of performing the first method than the one described (zinc, nickel, and cobalt being absent) would be to precipitate the aluminum and manganese by ammonium sulphide in the filtrate from the first ferric oxide precipitate; then filtering, dissolving in hydrochloric acid, separating alumina by precipitating with ammonia, boiling off excess; titrating the filtrate for manganese; filtering off the precipitated manganese dioxide; and adding filtrate to the main lime and magnesia solution (which has meanwhile been evaporated down) to recover the lime and magnesia (if any) carried down by the ammonium sulphide precipitation of the alumina and manganese. But, as before stated, the manganese dioxide precipitate carries down magnesia; but doubtless not when the magnesia present is small in amount as would be the case here. This point also, however, must be tested by experiment.

The Särnström reaction may evidently also be made use of in zinc ores for separating iron, alumina, and manganese from zinc, previous to titration of the latter with ferrocyanide. The method at present most in use, at least in the West, seems to be that of von Schulz and Low. But Mr. Bertrand Hinman finds their method inapplicable to eastern ores (on account of the insolubility of these ores, and also on account of the higher percentage of iron which makes the separation from zinc by ammonia and ammonium chloride an incomplete one) except certain modifications be adopted. Mr. George C. Stone, however, finds that even with these modifications the method does not work with New Jersey ores, and originates another method in which the iron and aluminum are separated from the manganese and zinc by precipitation with barium carbonate; and the latter titrated with ferrocyanide, manganese being determined in a separate portion, and the zinc then estimated by difference. Very accurate results are obtained by this method, but it would be just as accurate and convenient to apply Särnström's method as follows: Obtain the ore in hydrochloric acid solution. If not enough iron be present add ferric chloride solution in sufficient

[1] This Journal, 17, 473.

amount. Add about seven grams ammonium chloride; dilute to 300 cc.; neutralize in the cold with sodium carbonate till the liquid loses its transparence as previously described; bring to a boil and boil a minute; add one cc. sodium carbonate solution and mix; titrate for manganese with permanganate; filter from the mixed iron and manganese precipitate (according to Crookes, page 200, no zinc comes down with the manganese dioxide precipitated in this way) and wash with hot water; and titrate the filtrate with ferrocyanide for zinc. Instead of filtering and washing the mixed ferric oxide and manganese dioxide precipitate, however, it would be better to dilute to a definite volume, and, after mixing, decant through a filter an aliquot portion.

The writer takes this opportunity to make a few additional remarks on the determination of phosphorus in steel and cast iron. In a recent paper on that subject he advocated the use of double filters of Schleicher and Shüll's No. 579 or 589 black ribbon for the filtration of the yellow phosphomolybdate precipitate by aid of the pump, using the same filters for a number of different filtrations in succession. To this suggestion he wishes to add that these filters can very well be also used again the following day, or after having been dried out, for the same purpose; but that, for such an extended use, the number 589 black ribbon answers better than No. 579. The filters should not be unfolded when placed away for another use.

In filtering from the undissolved zinc through cotton wool, as in the method described in the article referred to, the same cotton wool may be made to answer for two consecutive filtrations, provided the percentage of phosphorus in the second of the two be not too low (under 0.05 per cent.). Below 0.05 per cent., fresh cotton should be used so as to get as rapid a filtration as possible. Several uses of the same filter clogs it considerably. Instead of performing this filtration by the pump, it is more convenient, owing to the extreme quickness and facility with which the liquid is drawn through the cotton wool, to use the mouth, by means of a clean rubber tubing of convenient length connected with the filtering flask.

Twenty-five cc. sulphuric acid (two of water to one of acid) was suggested for acidification of the phosphorus solution pre-

vious to the addition of a mustard-spoonful of zinc. If with the zinc in use it is found that this amount of acid dissolves it too quickly, or not quickly enough, the proper amount of acid to be used is found by varying the quantity added by one or two-tenths cc. If, for instance, twenty-five cc. are found to dissolve the zinc too quickly, so that the color of the reduced solution is only wine colored instead of green, as it should be, then 24.9 cc. will usually be found the right quantity for use on every occasion. It should perhaps be pointed out to those who have never used the Emmerton process that in titrating the reduced solution, the end point of the titration does not for some reason manifest itself with such suddenness as in the reductor process, and care must therefore be taken to note that the pink coloration is a distinct and permanent one.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CINCINNATI.]

LI. THE USE OF ALUMINUM FOR CONDENSERS.

BY T. H. NORTON.

Received January 18, 1897.

IN connection with the extended use of aluminum in this laboratory for various forms of apparatus, water-baths, air-baths, Bunsen burners, hot water filtering funnels, etc., it seemed desirable to study the availability of the metal for condensation processes.

For this purpose a condenser was constructed as follows: The outer jacket was of glass; the inner tube was of aluminum and possessed the following dimensions: length, 122 cm., external diameter, one cm., inner diameter, eight and one-half mm., weight per meter, twenty-nine grams. At a distance of fifteen cm. from the end, the tube was bent at right angles. This permitted of connection with a distilling flask, without allowing the condensing vapors to come in contact with any substance but aluminum. It might be mentioned here that in order to bend an aluminum tube of these dimensions satisfactorily, it is necessary to fill it with molten lead, and further, that several distillations with water are requisite in order to remove completely slight traces of lead adherent to the surface of the aluminum, after this operation.

The method of testing the condenser was to distil a measured

[1] Read before the American Chemical Society at the Springfield Meeting.

quantity of a liquid from the glass flask, used as a still, collect the distillate in glass, evaporate it from weighed platinum dishes and note the weight of the ignited residue, thus ascertaining whether there was any appreciable attack on the aluminum. Nothing was attempted beyond the ordinary precautions for preventing dust from contaminating the distillates.

The liquids first employed were organic. In each case 500 cc. were distilled, and the weights of the residue left on evaporating the distillate noted. The following results were obtained:

Liquid.	Residue from 500 cc.
Ethyl alcohol (specific gravity 0.809)	0.001 gram.
Benzene	0.0016 "
Nitrobenzene	0.0004 "
Chloroform	0.0002 "
Ethyl ether	0.0000 "
Acetone	0.0001 "

In all these cases it was evident that very rapid distillation could be carried on with an exceedingly short tube, on account of the high conductive power of the aluminum. The residues obtained showed that there was practically no attack upon the aluminum.

The deportment of the metal towards steam was next studied, and here it was deemed wise to establish in all cases comparative experiments with glass and block tin. The glass condenser tube used for this purpose was eighty-four cm. long and had an inner diameter of sixteen mm.; the tin condenser tube was 305 cm. long and had an inner diameter of twenty-one mm. With the exception of differences in the superficial surface for condensation, other conditions were essentially identical. Three series of distillations were carried on with the three following samples of water:

A. Hydrant water (Ohio River water), containing much impurity.
B. " " " " " " less "
C. Distilled water.

In all cases 500 cc. were employed. The following residues were obtained:

	Aluminum.	Block tin.	Glass.
A	0.0112	0.006	0.0118 gram.
B	0.0032	0.0028	0.0091 "
C	0.0035	0.005	0.008 "

A check determination on the amount of dust collecting in the platinum dish during the time for evaporation, showed it to be 0.0002 gram after ignition.

These results would show that as far as purity of the product is concerned, aluminum possesses about the same advantages over glass as tin, in connection with the distillation of water. In lightness and conductivity it exhibits marked superiority to the tin.

For use with neutral organic liquids it is well adapted, more especially in the distillation of low boiling substances such as ether. Here also the high thermal conductivity, as well as the absence of brittleness, are factors in its favor as compared with glass.

Mr. R. W. Hochstetter rendered valuable assistance in the determination of the above data.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CINCINNATI.]

LII. ON THE VOLATILITY OF CERTAIN INORGANIC SALTS.

BY T. H. NORTON AND D. M. ROTH.

Received January 18, 1897.

IN connection with some experiments on the volatility of sodium borate and sodium fluoride, carried on in this laboratory, it was thought advisable to make use of the method employed for certain salts by Bunsen nearly thirty years ago, but, as far as we can find from the literature, not used since then. This method consists in noting the time required for the volatilization of 0.01 gram of the substance under examination, in the form of a bead in a loop at the end of a platinum wire, after introduction into the hottest part of the Bunsen flame.[1] The disappearance of color when the substance is completely volatilized is marked and sudden. Naturally, great care must be observed in assuring, for purposes of comparison, identical conditions of location in the flame, temperature of the flame, etc. The method is of course applicable to such compounds only as impart color to the flame. Following Bunsen's example, the time required for the volatilization of 0.01 gram of sodium chloride was taken as unity. In this connection the volatility of most of the

[1] *Ann. Chem.* (Liebig), **138**, 263.

salts studied by Bunsen was redetermined and the following additional salts were examined for the first time: Borax, sodium fluoride, potassium fluoride, and barium chloride. The results of all determinations are tabulated below. Bunsen's published figures are given in a separate column. Slight variations from his results are to be noticed in most cases. The material employed was the purest obtainable. Duplicate determinations always gave concordant results:

Salt.	Time of volatilization of 0.01 gram. Seconds.	Sodium chloride as unity. N. and R.	Bunsen.
Sodium chloride	13	1.00	1.00
Sodium sulphate	130	10.00	15.04
Lithium carbonate	130	10.00	8.74
Potassium sulphate	87.5	6.73	7.89
Sodium carbonate	95.5	7.38	7.50
Potassium carbonate	47	3.61	3.23
" chloride	12	0.923	0.776
" bromide	7	0.538	0.487
" iodide	5.5	0.423	0.352
Sodium borate	215.5	16.54	....
" fluoride	104.5	8.04	....
Potassium fluoride	39.5	3.04	....
Barium chloride	1560.0	120.00	....

Tests were also made with calcium chloride, strontium chloride, and magnesium chloride. All three underwent decomposition, leaving a non-volatile, alkaline residue. Calcium sulphate and calcium fluoride were likewise tested. In both cases, although a slight coloration was imparted to the flame, there was no loss of material capable of detection by the balance.

COLOR REACTIONS OF NITRIC AND CHLORIC ACIDS WITH CERTAIN AROMATIC BODIES.[1]

By E. C. Woodruff.

Received January 8, 1897.

THE object of this research was to find some new practical tests for nitric and chloric acids, more especially tests that would differentiate the two both in mixtures and separately. The latter object has been attained several times over. The former is more difficult for several reasons. In general, chloric

[1] A thesis presented for the degree of Master of Science to the Council of the Graduate School of the University of Michigan, June, 1896. Communicated by O. C. Johnson.

acid produces a darker color reaction than nitric, in some few cases sufficiently so as to indicate chlorates in the presence of nitrates, in almost all cases enough darker to completely mask the nitrate effect. In some cases the effects are indistinguishable. Still two methods will be given later whereby the nitrate effect can be made to predominate, and best of all, one test has been found that, properly manipulated, accomplishes the desired result very well.

THE DIMETHYL ANILIN TEST.

The general method of procedure was as follows: About one cc. of the test solution, generally a solution of two grams of the aromatic substance in 100 cc. of concentrated sulphuric acid, was placed in a dry and clean test-tube and one drop of the nitrate, chlorate, or other inorganic salt solution was added. The whole was agitated and set aside until cold and the color fully developed. Thereupon a slight excess of a strong solution of potassium hydroxide or ammonium hydroxide was very slowly added, and, after standing a little while, enough water was added to redissolve any precipitate that might have formed, if it proved to be soluble. The color was noted at three stages, before and after neutralization, and after dilution. Generally the dilution did not weaken the color, as in most cases the precipitate was coloring matter in contact with a saturated solution of the same.

The organic substances selected for the tests are fairly typical of the main groups of the aromatic series. At least of those groups that present color reactions, *i. e.*, those bodies containing hydroxyl groups, or amido groups, or both. The following is a classified list:

PHENOLS:

Monoxybenzene: Phenol, $C_6H_5.OH$.

Dioxybenzene: $C_6H_4.(OH)_2$.

Pyrocatechol, (1 : 2); Resorcinol, (1 : 3); Hydroquinone, (1 : 4).

Trioxybenzene: $C_6H_3.(OH)_3$.

Pyrogallol, (1 : 2 : 3).

CRESOLS:

Monoxytoluene: $C_6H_4.CH_3.OH$.

Dioxytoluene: $C_6H_3.CH_3.(OH)_2$.

m-Cresol, (1 : 3). Orcinol, (1 : 3 : 5).

OXYACIDS:

Monoxybenzoic acid: $C_6H_4.OH.CO_2H$.

Trioxybenzoic acid: $C_6H_2.(OH)_3.CO_2H$.

Salicylic acid, (1 : 2). Gallic acid, (1 : 3 : 4 : 5—CO_2H in 1).

α-NAPHTHOL, $C_{10}H_7.OH$.

ALIZARIN, Dioxyanthroquinone, (1 : 2). $C_6H_4.(CO)_2.C_6H_2.(OH)_2$.

AMINES:

Amidobenzenes:

Anilin, $C_6H_5.NH_2$. Dimethylanilin, $C_6H_5.N(CH_3)_2$.

Acetanilid, $C_6H_5.NH.CO.CH_3$.

Diphenylamin, $(C_6H_5)_2NH$.

Amidotoluenes: $C_6H_4.CH_3.NH_2$.

Orthotoluidin, (1 : 2). Paratoluidin, (1 : 4)

Amidophenols:

Diamidophenol, $C_6H_2.(NH_2)_2.OH$.

Paramidometacresol, or "metol" $C_6H_3.CH_3.OH.NH_2$.

α-NAPHTHYLAMIN, $C_{10}H_7.NH_2$.

Table No. 1 gives in condensed tabulated form the reactions of these test solutions potassium nitrate, potassium chlorate, potassium bromate, potassium iodate, potassium bromide, potassium iodide, and a mixture of potassium chloride and nitrate. The colors are indicated thus:

V-violet; I-indigo; Bl-blue; Gr-green; Y-yellow; O-orange; R-red; W-white; Gra-gray; Br-brown; Pur-purple; Car-carmine; Cri-crimson; Pk-pink; Ch-cherry; Blo-blood red; YBr-yellowish brown; etc.

The modifying adjectives are indicated thus:

s-strong; l-light; d-dark; v-very; m-muddy.

This gives a means of expressing nearly 300 reactions on one page.

In making out this table the general method of experimentation as given on page 157 was followed. The phenol solution was of thirty per cent. strength. It was made from crystals that had somewhat reddened. Still it gave a perfectly white solution

that at the end of one month showed not the slightest discoloration. It is one of the strongly recommended tests for nitrates, not being interfered with by bromides nor iodides nor any of the metals if the proper alkali be chosen for neutralization. The same can be said of the salicylic acid test. The solution consisted of one gram of sodium salicylate dissolved in forty cc. of concentrated sulphuric acid. These two tests depend on the formation of ammonium or potassium picrate, giving a solution of a strong yellow or greenish yellow color. Another method of performing the phenol test deserves mention. It is probably more delicate though not so quick-acting as the one first given. The final result is the same. Into a dry test-tube is put one cc. of concentrated sulphuric acid. On this is very carefully floated a layer of a saturated water solution of phenol, not more than one-half cc. Now a drop of the unknown is allowed to fall gently on the upper layer, generally immediately producing a strong brown ring. After standing for some time the whole is shaken and neutralized, when a strongly picrate-colored solution indicates a nitrate. Chlorates give a brownish yellow instead of a greenish yellow. This serves as a distinguishing test in solutions where only one of the two is present.

The di- and trioxybenzenes furnish still more delicate tests for both nitrates and chlorates, but unfortunately give the same result with both as far as color is concerned, though perhaps a somewhat stronger effect with chlorates. Hydroquinone is the best of the four by far, giving a clear white solution possessing comparatively remarkable keeping qualities. A three per cent. solution was used. The resorcinol keeps well but gives a light brown solution, making it unsuitable for delicate tests unless freshly prepared. The pyrocatechol and the pyrogallol solutions do not keep at all if allowed access to the air. In these cases the test was performed by adding a minute crystal of the pyrogallol or the pyrocatechol to one cc. of sulphuric acid already in the test-tube, and going through the operations somewhat rapidly. The resorcinol used was two per cent. strong. All four under the proper conditions give the same result, a yellow solution with either a brown or a green tinge.

The monoxytoluenes give practically the same result as the phenols, both as regards delicacy and certainty of result, and,

although the test solution itself is somewhat brownish, still the effect of this on the final color is absolutely nothing at all, which cannot be said concerning any color in the test solutions where mere oxidation and not nitration is concerned.

The strength of the orcinol solution was two per cent. It was light brown in color but kept well and gave good results. Its special value was in the different results it gave while still acid with nitrates and chlorates, strong yellow red with the former and strong green with the latter.

The gallic acid solution, one per cent., was a disappointment. Although it gave a clear white test solution, and strong color reactions, with the nitrates especially, still it would give some color with bromides and iodides, and sometimes on neutralization without having any other salt added to it.

Naphthol and naphthylamin, both one per cent., gave strong clear tests. The naphthylamin distinguishes nitrates and chlorates as per table.

The alizarin was a bleaching test. Alizarin was added to sulphuric acid until a pink or light crimson solution was obtained. This, plus water, would give a bright yellow, plus potassium hydroxide, would give a strong purple, but nitrates, chlorates, bromates, iodates, and iodides so affect the sulphuric acid solution that addition of potassium hydroxide gives a colorless, or at the most, a very light purple result.

Acetanilid, one per cent, is sufficiently explained by the table.

Diphenylamin, four per cent., gave a light green solution which gradually darkened. This makes a fairly delicate test for nitrates, but there are several serious faults in its workings. First, it gives a rather poorly keeping solution. Second, it will not bear dilution or neutralization, so as to eliminate the effects of bromides and iodides, and so as to distinguish between nitrates and chlorates, even when only one of the two is present, nitrates, chlorates, bromates, and iodates all giving practically the same color. Third, it must be kept cool; heat alone, even the heat generated by adding a drop of distilled water to two or three of the solution may give the color supposedly due to a nitrate. Heating changes it first to green, then to a blue, and finally to dense black flakes in a colorless liquid in which water no longer produces a muddy brown precipitate as before.

The anilins and the toluidins will be treated later, after the comparative indices.

"Amidol," or diamidophenol hydrochloride, one per cent., makes a very delicate quick-acting test in acid solution, the test solution keeping very well considering its susceptibility to atmospheric oxidation. This latter sensitiveness somewhat spoils the effect of neutralization unless the test is performed rapidly.

"Metol," or paramidometacresol, one per cent., makes a test solution that resembles hydroquinone in its keeping properties and reactions.

Table No. 2 gives a comparative index for nitrates, and Table No. 3 a similar index for chlorates. These indices are arranged as follows: The first column contains the list of test solutions with its own colors marked. Of the remaining columns those to the left of the central double line contain the reactions on neutralization with potassium hydroxide, and those to the right on neutralizing with ammonium hydroxide. Fifteen drops of the test solution and one drop of a five per cent. solution of the nitrate or chlorate gave reaction (1); six drops of water gave reaction (2); an insufficient quantity of the neutralizing agent, reaction (3); an excess of the same, reaction (4); lastly, equal dilution with water, reaction (5). The remaining columns indicate the comparative strength of the color produced after the reaction whose number occurs at the top. A indicates the strongest color, B the next strongest, and so on. In each case the comparison is made only with the other colors in the same column. The fact that any one reaction is marked A means only that it gave the darkest color, not that it gave the clearest, most distinctive, or even most delicate test. The addition of water in the second reaction was for the purpose of preventing the intense heating effect produced by dropping strong potassium hydroxide solution into concentrated sulphuric acid. In some cases this modified to a considerable extent the reaction as given in the General Table. Further important details will appear on examining the indices. Especially significant is the fact that the strongest tests for nitrates were not always the strongest for chlorates even when they gave the same color, and vice versa.

By far the most interesting and most valuable results came from the study of the anilins and the toluidins. Table No. 4 shows the reactions of ten combinations of these substances, both as to the actual color produced and the comparative strength of the colors at different stages. A great many peculiar features came out in this series. The green and blue effects in the chlorate series gradually faded away leaving brown. A little water might restore the color which would soon again fade away. Again addition of water might reproduce the color which would more slowly disappear. Finally, considerable dilution would restore the color so that it would fade quite slowly but permanently. The green and blue effects to which reference are made are the ones in the column headed $\overset{(4)}{H_2O}$. Effects of the same nature, but during the process of neutralization, were noticed in the experiments with mixtures of potassium nitrate, with potassium chloride or potassium chlorate, as per table. In all cases where orthotoluidin was used a strong green appeared while adding potassium hydroxide. Sometimes it persisted for quite a while after complete neutralization. All traces of green eventually disappearing, addition of water reproduced the color which faded and was again reproduced as above.

The tests to which particular attention is called are those in horizontal lines (8) and (9). Notice the difference in the first effect in all four cases. Test No. (9), it will be noticed, gives the much desired means of detecting a nitrate in the presence of chlorates, bromates, and iodates. The first operation is the important one. If the chlorate be not in too great excess the blood red color produced by the nitrate is sure to show. Below are given some data on the sensitiveness of this test. It will be noticed that though chlorides alone have no color effect, they very much intensify the nitrate effect. The best formula appeared to be:

Dimethyl anilin	2 drops.
Paratoluidine	0.2 grams.
Sulphuric acid	10 cc.

It gives a colorless solution that keeps well.

On the same page are given data on the sensitiveness of the phenol, salicylic acid, and hydroquinone tests for nitrates, and

the anilin test for chlorates. A remarkable feature about the last is the radical change in color on standing.

Two methods of removing or reducing the strength of chlorates in a solution containing nitrates have been experimented with.

(1). Acidify with sulphuric, add hydrochloric, and boil until on adding another drop of hydrochloric and boiling no yellow color appears. Now the phenol test can show the nitrate without the slightest trace of the brown color due to chlorates.

(2). Carefully evaporate just to dryness, add cold water not sufficient to redissolve all the chlorate, dilute, and use the dimethylanilin test. All the nitrate dissolves before an equal quantity of chlorate, and as the test is good for nitrates in the presence of the same bulk of chlorates, it will work even more surely with a less amount.

An actual experiment of this sort ran as follows: Twenty cc. of water was saturated with potassium chlorate at about 50° C. and one gram of potassium nitrate added. When the solution had cooled to the temperature of the room, some of the potassium chlorate had crystallized out. Still more potassium chlorate than nitrate remained in solution. One drop of this gave a dark brown test with traces of crimson. The chlorate masked the nitrate. But when some of the solution was diluted with four volumes of water, in spite of the fact that the chlorate exceeded the nitrate in the same ratio as before, one drop gave a strong crimson reaction, the chlorate effect being overlooked. Then the original solution was evaporated to dryness, the residue cooled, and agitated with ten cc. of cold water. Now a test showed strong crimson but with a brownish tint. On adding four volumes of water to some of this solution the brown tint did not appear, only the crimson nitrate effect.

The dimethylanilin test has proved to be practically an absolute test for nitrates. The test has been successfully worked in the presence of each of the inorganic salts commonly met with, even the most powerful oxidizing and reducing agents. Of the metals, Sn'', Sb''', Fe'' are the only ones that tend to spoil the test by reducing the nitrate. Oxalic, acetic, hydrosulphuric, iodic, and arsenious acids seemed to exert a similar influence on the test. However, the only one of these two lists that was

always deleterious was Fe''. $K_3Fe(CN)_6$, $K_4Fe(CN)_6$, and KNO_2 seemed to give a pink to crimson color that might have been due to impurities in the reagents. Addition of nitrate, however, immediately strengthened the color to such an extent as to obviate any difficulty on that score. The color produced by potassium ferrocyanide was very feeble, which result seemed to uphold the suspicion of impurity in the other cases. Potassium chloride, potassium bromide, potassium iodide, chlorine, bromine, iodine, and potassium thiocyanate seemed to have no effect whatever, excepting that potassium chloride strengthened the nitrate reaction. Similarly potassium chromate, potassium dichromate, potassium arsenate, and potassium permanganate presented no color reaction of their own, but seemed to help the nitrate in its reaction. Potassium permanganate lost its own color when added separately to the test solution. As mentioned above, potassium chlorate, bromate, and iodate do not interfere with the test under ordinary circumstances.

In view of these various results, to get the maximum efficiency out of the test, would require the following method of procedure:

To the unknown add potassium chlorate, if not already present, then some hydrochloric acid, and boil. This will oxidize all the reducing agents that might otherwise be harmful, without introducing enough excess of potassium chlorate to injure the result.

TABLE NO. 1. GENERAL INDEX OF REACTIONS.

Test solution of	KNO_3.	KOH.	$KClO_3$.	KOH.	$KBrO_3$.	KOH.	KIO_3.	KOH.	KBr.	KOH.	KI.	KOH.	KCl and KNO_3.	KOH.
Phenol	Y	sGrY	RY	dGrBr	RY	lYBr	sRY	lYBr	lY	W	Md	W	Y	GrY
Pyrocatechol														
Resorcinol	Y	Y	BrY	lBr	BrY	lBr	MdBr	lBr	lY	W	Md	W	Y	Y
Hydroquinone	sYR	YR	YBr	YBr	YBr	YBr	MdBr	YBr	W	W	MdGra	W	YBr	YBr
Pyrogallol	sYR	sYBr	vdBr	vlBr	YBr	lBr	sBr	lBr	lY	W	Md	W	sYR	YR
Cresol	Y	sY	BrY	dGrBr	BrY	vsRBr	MdBrY	vsRBr	Y	vvl	Md	vvl	Y	sY
Orcinol	sYR	sYR	sGr	YBr	sGr	Br	dMd	sBr	W	W	Md	W	sYR	sY
Salicylic acid	lY	sY	dYBr	sBr	RY	sBr	RY	sBr	lY	W	Md	W	lY	sY
Gallic acid	sYR	sYBr	Y	lY	Y	W	MdGr	lY	W	lPkBr	Md	lPkBr	RY	Y
a-Naphthol	sBrY	sY	sBrY	Br	sRY	Br	MdGr	Y	W	W	Md	W	sBrY	Y
Alizarin	Y	W	Y	W	BrY	W	Y	W	Y	Pur	Md	W	Y	W
Anilin oil	dRBr	Y	vsBl	sPur	dBl	lBr	sRBr	lBr	RY	W	Md	W	sPurBr	Br
Dimethylanilin	RY	sY	Y	vlBr	Y	vlBr	sRY	vlBr	Y	W	Md	W	sRY	sY
Acetanilid	lY	sY	dRBr	dGrBr	YBr	Br	YBr	lBr	RY	W	Md	W	lY	Y
Diphenylamin	sBl		sBl		sBl		sBl		sGr		Md		sBl	
Orthotoluidin	sYBr	Y	sBl	PurBl	sBl	lBr	MdsBl	lBr	YBr	W	Md	W	sBrPur	GrY
Paratoluidin	vdBr	Br	vsBr	Br										
"Amidol"	vsYR	YBr	sPurR	YGr	sR	YGr	vsPurR	YBr	Y	lBr	Md	lBr	RY	YBr
"Metol"	YR	YBr	Y	YBr	YR	Y	sYR	sYBr	vlY	W	Md	W	Y	YBr
a-Naphthylamin	dPurGr	Y	dYR	dBr	dYR	dBr	MdBr	YBr	W	W	Md	W	dPurR	RY

TABLE NO. 2. COMPARATIVE INDEX FOR NITRIC ACID.

Test solution of	(1) KNO_3.	(2) H_2O.	(3) KOH.	(4) KOH.	(5) H_2O.	(4)	(5)	(1) KNO_3.	(2) H_2O.	(3) NH_4OH.	(4) NH_4OH.	(5) H_2O.	(1)	(2)	(4)	(5)
Phenol, W.....	Y	lY	vlY	sY	sY	E	E	Y	lY	vlY	sY	sY	C	E	D	C
Pyrocatechol																
Resorcinol, lBr	Y	Y	O	sY	sY	E	E	Y	Y	sY	sY	sY	C	E	D	C
Hydroquinone, W	vdRBr	RY	dBrR	vdBr	vsYBr	C	C	vdBr	sRBr	dRBr	vsRBr	sYBr	A	C	B	C
Pyrogallol.....	BrY	vlY	dBr	vdBr	sBr	C	C	vdBr	vdBr	vdBr	vsBr	sYBr	A	B	A	C
Cresol																
Orcinol, lBr	dRY	O	dYR	dRY	sBrY	D	D	sBrY	YBr	O	sRB	sYBr	B	D	B	C
Salicylic acid, W.....	lY	vlY	vlY	sY	sY	E	E	lY	W	sY	sY	sY	D	G	D	C
Gallic acid, vlY.....	vsBr	dYBr	Br	vdBrR	sBrY	C	D	vdBr	vdBr	dBr	sYBr	sYBr	A	B	C	C
a-Naphthol, lBr	s GrBr	O	lY	dRY	sO	D	C	sGrY	YBr	Y	sRBr	sYBr	A	B	C	C
Alizarin, sPk.....	lY	lY	vlY	vlPur	vlPur	H	H	lO	lY	lY	vlY	W	C	F	F	F
Anilin oil, vlY.....	vdBrR	Gra	lYBr	MdBr	Y	D	E	vsBr	sBlGra	MdY	MdY	GrY	A	B	C	D
Dimethylanilin																
Acetanilid, W.....	Y	Y	Y	sY	sY	F	E	Y	Y	Y	Y	GrY	C	E	E	D
Diphenylamin, Gr....	vsBl					(1) A		vsBl					A			
Orthotoluidin, Br.....	vdRBr	vdBr	MdBr	MdBr	Y	D	E	vdR	sYBr	GrY	GrY	GrY	A	C	D	D
Paratoluidin																
"Amidol," vl.....	vdBrR	dBlo	vdBrR	vdBrR	vvsR	A	A	vdR	vsBlo	vvdBr	vvsBr	vvsBr	A	B	A	A
"Metol," W.....	Y	BrY	O	sYR	sYBr	D	D	Y	lO	RBr	vvsBlo	vsR	C	E	A	B
a-Naphthylamin, lBr..	vdBr	dYBr	vdBr	vdYBr	vsRBr	B	B	vdBr	vsYBr	vvdBr	vsRBr	vsYBr	A	B	B	C

TABLE NO. 3. COMPARATIVE INDEX FOR CHLORIC ACID.

Test solution of	(1) $KClO_3$.	(2) H_2O.	(3) KOH.	(4) KOH.	(5) H_2O.	(1)	(2)	(4)	(5)	(1) $KClO_3$.	(2) H_2O.	(3) NH_4OH.	(4) NH_4OH.	(5) H_2O.	(1)	(2)	(4)	(5)
Phenol.....	Y	Y		dGrBr	vlBr	D	D	B	D	Y	Y	sBr	YBr	lBr	D	D	C	D
Pyrocatechol.....																		
Resorcinol.....	sY	Y		lBr	W	D	D	E	F	vsBr	vsBr	vsBr	vsBr	sBr	A	A	A	B
Hydroquinone...	sBrY	Br		YBr	sY	C	C	C	C	sBr	sBr	vsBloBr	vvsBr	vdBr	B	B	A	B
Pyrogallol.....	vdBr	vdRBr		dYBr	vsBr	B	B	B	E	vsBr	vsBr	vsBr	vsBr	sBr	A	A	A	B
Cresol.....																		
Orcinol.....	MdsGr	MdGr		vdGrBr	dBr	C	C	A	B	vsBrGr	MdBr	BrY	sO	sB	A	C	C	C
Salicylic acid	Y	Y		YBr	vlBr	D	D	C	D	Y	Y	BrY	Br	lBr	D	D	C	C
Gallic acid.....	sGrBr	Br		YBr	Br	B	C	C	C	vsBrY	sBrY	sO	sO	sGrBr	A	B	C	B
a-Naphthol	sYBr	Br		dYBr	Br	B	C	B	C	vsBrY	sBrY	BrY	vsBr	sGrBr	A	B	B	B
Alizarin.....	lY	vlY		W	W	E	E	F	F	lY	lY	lY	W	W	F	E	E	E
Anilin oil.....	vdBl	vdBl		MdBr	RPur	A	A	B	B	vdBl	vdBl	MdBr	MdBr	sGra	A	A	A	C
Dimethylanilin ..																		
Acetanilid.....	lY	O		lBr	vlY	E	D	D	E	BrY	sBrY	YBr	YBr	lBr	D	C	C	D
Diphenylamin ...	vsBl					A				vsBl					A			
Orthotoluidin...	vdBl	vdBl		MdPur	sBlPur	A	A	A	A	vsBl	vsBl	MdPurGra	sBl	vsBl	A	A	B	A
Paratoluidin																		
"Amidol".....	lBr	sCh		dYGr	sGrBr	E	B	B	B	lY	vsBlo	vsBr	vsBr	vdGrBr	F	A	A	A
"Metol".....	lO	lY		YBr	vlBr	E	D	C	D	Y	lY	vsBloBr	vsRBr	dBr	F	E	A	B
a-Naphthylamin..	sR	sYR		vdYBr	dBr	B	C	A	B	sRY	sBrY	vsBr	MdvvsBr	vdBr	B	B	A	B

TABLE NO. 4. INDEX FOR THE ANILINS AND TOLUIDINS.

Fifteen drops of test solution of	1 drop 5 per cent. KNO_3.	6 drops H_2O.	KOH.	H_2O.	(1)	(4)	1 drop 5 per cent. $HClO_3$.	6 drops H_2O.	KOH.	H_2O.	(1)	(4)	1 drop each KCl KNO_3.	4 cc. H_2O.	KOH and H_2O.	(1)	KNO_3 and $KClO_3$.	H_2O.	KOH and H_2O.	(1)
(1) Anilin	vdBr	Br	MdBr	Y	A	B	vvsBl	vdBr	MdBr	PkBr	A	A	vsBr	Br	Y	A	vsBl	dBr	BrY	A
(2) Orthotoluidin.	vvdBr	vsRBr	MdBr	Br	A	A	vvsBl	sCri	MdBr	GrBl	A	Bl	vsPurBr	sBr	Gr	A	vsBl	dBr	Gr	A
(3) Paratoluidin	vdBr	Br	Md Br	Y	A	B	vsBr	Br	MdBr	Br	B	C	vsRBr	Y	Y	A	vsBr	YBr	Y	A
(4) Anilin and orthotoluidin	vdBr	sBr	MdBr	Y	A	B	vvsBl	sCri	MdBr	GraBl	A	B	vsPurBr	Br	Gr	A	vs Pur	dR	Br Gr	A
(5) Anilin and paratoluidin	vsCri	lBr	MdY	Y	C	B	vsBl Pur	sBr	MdBr	lBr	B	C	vsCri	Y	Y	A	vsCri Pur	R	BrY	A
(6) Anilin and both toluidins	vvs-Blo	sBr	MdBr	Y	A	B	vvsBl	vsCri	MdBr	GraBl	A	B	vsCri	RY	YGr	A	vsPur Cri	dBr	Br YGr	A
(7) Dimethylanilin	sYO	O	MdY	Y	C	B	Y	YGr	MdBr	lBr	C	C	sYCri	O	Y	B	sYCri	O	Y	B
(8) Dimethylanilin and orthotoluidin	vsBr	Br	MdY	Y	B	B	vs BlGr	vs RBr	MdBr	Br	B	B	vsRB	R	Gr	A	vsBr	R	Gr Br	A
*(9) Dimethylanilin and paratoluidin	vsBlo	lBr	MdY	Y	C	B	vsBr	sRBr	MdBr	lBr	B	C	vsBlo	Y	YBr	*A	vsBlo	YBr	BrY	A
(10) Dimethylanilin and both toluidins	vsBlo	lBr	MdY	Y	A	B	vvs BlPur	sRBr	MdBr	lBr	A	C	vsBlo	R	YBr	*A	vsBlo	R	BrY	A

FORMULAS USED IN PREPARING THE TABLE.

(1) Anilin ..... 4 drops
(2) Orthotoluidin ..... 4 "
(3) Paratoluidin ..... 0.4 gram
(4) Anilin ..... 2 drops
Orthotoluidin ..... 2 "
(5) Anilin ..... 2 "
Paratoluidin ..... 0.2 gram
(6) Anilin ..... 2 drops
Orthotoluidin ..... 2 "
Paratoluidin ..... 0.2 gram
(7) Dimethylanilin ..... 4 drops
(8) Dimethylanilin ..... 3 "
Orthotoluidin ..... 2 "
(9) Dimethylanilin .... 2 drops
Paratoluidin ..... 0.2 gram
(10) Dimethylanilin .... 2 drops
Paratoluidin ..... 0.2 gram
Orthotoluidin ..... 2 drops

In all cases ten cc. of concentrated sulphuric acid were used.

Table No. 5. Sensitiveness of Various Tests.

Dimethylanilin, (9) Table 4.			Ten drops of test solution and one drop 5 per cent. KCl and KNO_3 as before.	In ten minutes	Phenolsulphonic Acid.			Salicylic Acid.		
Ten drops of test solution and one drop of KNO_3 of	In a few seconds.	In ten minutes.			15 drops of test solution and 1 drop KNO_3 as before, two minutes.	Three hours.	+KOH.	Two minutes.	Three hours.	+KOH.
5 per cent.	sCri	vsCri	sCri	vvsBlo						
1 " "	Pk	sPk	Cri	vsBlo	lY	Y	sY	lY	Y	sY
0.1 " "	vlPk	lPk	Pk	sBlo	vvlY	vlY	lY	W	lY	lY
0.01 " "	vvlY	vvlY	vlPk	lPk	W	W	W	W	W	W
0.001 " "	vvlY	vvlY	vvlPk	lPk						

Hydroquinone.			Diphenylamin.			Anilin test for chlorates.	
15 drops of a one per cent solution and 1 drop KNO_3 of	After five minutes.	After one-half hour + KOH.	Fresh solution { 0.1 gram / 10 cc. H_2SO_4.		15 mm. No. 6, Table 4. + 1 mm. of	2 min.	15 min.
			15 mm. + 7 mm.	2 seconds.			
			1 per cent. KNO_3.	vvsBl	1 per cent. $KClO_3$	vvdBl	dBrR
			0.1 per cent.	6 seconds.	0.1 per cent.		
0.1 per cent.	Br	BrY	KNO_3.	sBl	$KClO_3$	Bl	lBr
			0.01 per cent.	0.5 minute.	0.01 per cent.		
0.01 per cent.	lBr	vlY	KNO_3.	lGrBl	$KClO_3$.	W	vvvlBr
			0.001 per cent.	1 minute.			
0.001 per cent.	vlBr	W	KNO_3.	No change.			

NOTE.

The Lavoisier Memorial.—It is doubtless well known to a majority of the members of the American Chemical Society that it is proposed to erect a monument in Paris to the memory of the illustrious Lavoisier, and dedicate it at the time of the next French Exposition, in 1900.

The honor of suggesting this monument, or at any rate, the erection of it by popular subscription among chemists, appears to belong to the United States, as Dr. Gustavus Hinrichs, of St. Louis, first called public attention to the propriety of doing homage to the memory of the savant in this manner.

The work is being conducted under the auspices of the French Academy of Sciences, and committees have been formed in this country, England, and Germany, as well as in France, to raise funds to defray the expense of erecting a suitable monument. It is hoped that the amount secured will be sufficient to provide a monument worthy the name of Lavoisier.

Unfortunately, the committee for the United States was slow in beginning its work, but there is yet ample time to do all that is necessary if a proper response be made to the solicitations of the men who have agreed to do the work among American chemists and other friends of science. Dr. Hinrichs was made the delegate of the French Academy for the United States. He has asked the following named chemists to serve as an American committee, to whom contributions should be made:

Jasper L. Beeson, A.M., Ph.D., late Professor of Chemistry in the Audubon Sugar School; Research Chemist for the Louisiana Experiment Station, Etc. New Orleans, Louisiana.

Charles Anthony Goessmann, Ph.D., LL.D., Professor of Chemistry at the Massachusetts Agricultural College; Chemist at the Hatch Experiment Station of the College; Chemist of the Massachusetts State Board of Agriculture, Etc. Amherst, Massachusetts.

Eugene W. Hilgard, Ph.D., LL.D., Professor of Agricultural Chemistry in the University of California; Director of the California Experiment Station. Berkeley, California.

Richard Watson Jones, M.A., LL.D., Professor of Chemistry in the University of Mississippi. University, Mississippi.

John Uri Lloyd, Professor of Chemistry in the Eclectic Medical Institute of Cincinnati; President (1887) of the American Pharmaceutical Association. Cincinnati, Ohio.

John H. Long, M.S., Sc.D., Professor of Chemistry and Director of the

Chemical Laboratories of the Schools of Medicine and Pharmacy of the Northwestern University. 2421 Dearborn Street, Chicago, Illinois.

John Ulric Nef, Ph.D., Professor of Chemistry and Director of the Kent Chemical Laboratory of the University of Chicago. Chicago, Illinois.

James Marion Pickel, A.M., Ph.D., Professor of Chemistry in the University of Alabama. University, Alabama.

Paul Schweitzer, Ph. D., Professor of Agricultural Chemistry and Chemist to the Agricultural Experiment Station, University of the State of Missouri. Columbia, Missouri.

William Simon, Ph.D., M.D., Professor of Chemistry in the College of Physicians and Surgeons of Baltimore, in the Maryland College of Pharmacy and in the Baltimore College of Dental Surgery. 1348 Block Street, Baltimore, Maryland.

Edgar F. Smith, Ph.D., Professor of Chemistry in the University of Pennsylvania; Director of the John Harrison Laboratory of Chemistry; President (for 1895) of the American Chemical Society. Philadelphia, Pennsylvania.

Eugene Allen Smith, Ph.D., State Geologist of Alabama; Formerly Professor of Chemistry, now of Mineralogy and Geology in the State University of Alabama. University, Alabama.

Henry Trimble, A.M., Ph.M., Professor of Analytical Chemistry in the Philadelphia College of Pharmacy; Editor of the American Journal of Pharmacy. 145 North Tenth Street, Philadelphia, Pennsylvania.

Francis Preston Venable, Ph.D., Professor of Chemistry in the University of North Carolina; Secretary (for 1896) of the Chemical Section of the American Association for the Advancement of Science. Chapel Hill, North Carolina.

Gustavus Detlef Hinrichs, M.D., LL.D., Professor of Chemistry, St. Louis College of Pharmacy; Delegate of the Academy of Sciences, of Paris, for the United States. 3132 Lafayette Avenue, St. Louis, Missouri.

The members of the committee have been provided with blanks and explanatory circulars, and have already sent out many to persons likely to contribute. It is hoped that all members of the American Chemical Society will feel interested in the project and will assist liberally. It should be stated that every dollar contributed will be sent to the treasurer of the fund, M. Gauthier-Villars, at Paris, as all expenses attending the collection here will be defrayed by the members of the committee.

J. H. LONG.

NEW BOOKS.

CHEMISTRY FOR ENGINEERS AND MANUFACTURERS. By BERTRAM BLOUNT and A. G. BLOXAM. VOL. II. CHEMISTRY OF MANUFACTURING PROCESSES. 8 vo. 484 pp. 1896. London: Charles Griffin & Co., L't'd. Philadelphia: J. B. Lippincott Co. Price, $2.50.

The first volume of this work, issued early in 1896, has been

reviewed in this Journal, 18, 745. The second volume is double the size of the first and contains, besides an index, a bibliography. In the latter we notice several books by American authors, but, unfortunately, many are wanting. Thus Sadtler's admirable work on "Industrial Organic Chemistry," which gives many processes connected with the topics treated of in the work before us is not mentioned. Yet the authors have endeavored to make the book attractive to American readers, and frequent references are made throughout to our methods and processes. The work is illustrated by over forty cuts and the general make up in type and paper is excellent.

There are eighteen chapters, and both inorganic and organic products, and their manufacture, are treated of.

Under the alkalies we notice an outline of the electrolytic preparation of caustic and other products, while the Solvay and LeBlanc processes receive their due share of attention.

Under the head of destructive distillition, water gas, and the enriched water gas used as an illuminant are very briefly considered. These processes do not find favor in England, though they have been greatly perfected there. Acetylene receives notice, but its position toward illuminating gas when manufactured from calcium carbide is still under trial. The enrichment of coal gas is on the increase, however, since we have a record of thirty candle power, as furnished to Edinburgh, and nearly as high to other towns. The enrichment of gas will undoubtedly be more generally practised the more gas is used as fuel, since the heating value is increased per cubic foot used, by the increase of combustible, due to added hydrocarbons.

The utilization of "basic slag" as a fertilizer is given space and a figure of the ball grinding mill used to reduce the slag to a fine powder is inserted. The Siemens tank furnace for glass manufacture is described and a figure showing cross section given. Very brief mention is made of the newer glasses for optical, thermal, and other scientific and industrial uses, whose manufacture in Germany has marked a decided advance.

Under the processes of sugar manufacture we find that of dextrose given, but no mention of Behr's method, whereby pure

anhydrous dextrose is commercially obtained by crystallization from aqueous solution.

The chapter on "Brewing and Distilling" is very short, being but an outline of the processes. This is also true of the two succeeding chapters on oils, resins, varnishes, and fats. The textiles and their bleaching are considered in a short chapter, while the theory of dyeing and dyestuffs are given considerable space. Paper, pigments, and paints form a couple of chapters. Leather and glue receive quite a proportionate amount of attention.

It is of course extremely difficult to condense so many and such varied topics into a book of this size, but the authors have discriminated on the whole wisely.

Above all things, it is to be noted with some satisfaction that chemical engineering problems are coming more to the front and that books of this character are multiplying. That the authors are live men the writer had an opportunity to judge from an inspection of a highly interesting exhibit by Mr. Blount, at the Institute of Civil Engineers. The apparatus was devised especially to meet the demands coming from engineers regarding important problems as the estimation of oxygen in copper, the quality of boiler scale produced by waters, etc.

He also had the pleasure of listening to an able lecture by Mr. Bloxam before an audience of gas engineers. The topic was the recovery of cyanogen compounds from gas works. The various lines of procedure for recovering these now most useful products were detailed as were also the uses to which the products could be put.

It is to be hoped that manufacturers, especially in the United States, will, through just such treatises, be led to see the value of chemical knowledge and skill for the proper control of their works and thus stimulate young men to undertake studies which will more fully fit them for responsible positions.

C. A. DOREMUS.

THE DEVELOPMENT OF THE PERIODIC LAW. By F. P. VENABLE, PH.D., F.C.S. Easton, Pa.: Chemical Publishing Co. 1896. viii + 321 pp. Square 12mo. Price, $2.50.

The author of this important work, who is Professor of Chemistry in the University of North Carolina, has already become

favorably known by his "Short History of Chemistry," (Boston, 1894.) When one undertakes to write the history of events that have taken place in several countries of Europe, it is a great advantage to be an American, as this insures more candor and impartiality than is likely to characterize a European author. Professor Venable shows extensive acquaintance with the literature of his subject and good judgment in the selection of materials.

In a prefatory sketch the author gives a condensed summary of the development of the periodic law, the details of which are elaborated in eight succeeding chapters; in this he expresses the feeling that the system is far from complete: "The close of this century calls loudly for another Lavoisier who shall interpret the facts won by such hard toil and place the science on the right track for another century of brilliant progress and discovery."

In the first chapter he discusses the hypothesis of Prout and the triads of Doebereiner, with the views of Berzelius, Dumas and others, respecting the numerical relations of the atoms. The latter topic is treated more at length in Chapter II. Then follows some account of Brodie's Ideal Chemistry, of the telluric screw of de Chancourtois, and of the law of octaves proposed by Newlands; the contributions of many minor lights to the general subject are not overlooked, as, for example, the propositions made by Kotikovsky, by Lenners, by Hinrichs (pantogen), and others.

Of course Lothar Meyer and Mendeléeff receive the most attention, and their share in founding the periodic law is most conscientiously given.

The writer of this can supply a single item from personal knowledge: the author of the anonymous paper on the Pairing of the Elements, which appeared in the American Supplement to the New York edition of the *Chemical News*, in 1869, was the late Professor Charles A. Seeley, of New York.

As one reads this valuable contribution to the history of an idea, one is struck with the number of persons who have contributed in a lesser measure to the general subject; thus, we find the names of Gibbes, Zängerle, Crookes, F. W. Clarke, Bayley, Carnelley, Rydberg, Bazaroff, Tchitcherine, Sutherland, Bassett, Flavitzky, and a host of others.

The work is not illustrated in the sense of containing pretty pictures of complicated apparatus copied from foreign books rather out of date, but it does contain representations of many diagrams, such as the spiral of von Huth, the diagrams of W. Spring, of W. Crookes, of Flavitzky, and the "generation tree" of Wendt.

A valuable feature of this work is the "Index to the Literature Relating to the Periodic Law," containing 267 titles. The book is well indexed.

This contribution to the history of chemistry will prove of use to all those interested in studying great questions which influence the progress of science. H. CARRINGTON BOLTON.

ROENTGEN RAYS AND PHENOMENA OF THE ANODE AND CATHODE. By EDWARD P. THOMPSON, M.E., E.E. Concluding chapter by PROF. WM. A. ANTHONY. New York: D. Van Nostrand Co. xvi + 190 pp. Price, $1.50.

This book is a mere compilation of 210 abstracts from various scientific journals and original memoirs. Mr. Thompson makes no attempt at classification or analysis, but has done the work hastily and superficially, by his own confession, apparently to meet the popular demand for illustrated books on this subject. There are many blunders, both in fact and in style, and the book will hardly commend itself to anybody who has access to one or two of the various scientific journals. Prof. Anthony's chapter is by far the best part of the book, as it gives a succinct and intelligible resumé of the various theories that have been advanced by Roentgen's discovery. It is to be regretted, however, that Hertz's researches on radiant electricity have received such scant attention; since they are not only the direct cause of the work of Lenard and of Roentgen, but also contain much that must be taken into account in all later speculations. It would also seem to the reviewer that Prof. Anthony does not do sufficient justice to those hypotheses which involve "free energy," not directly fastened to particles of substantial matter.

MORRIS LOEB.

THE CHEMISTRY OF DAIRYING. By HARRY SNYDER. viii + 156 pp. Easton, Pa.: Chemical Publishing Co. Price, $1.50.

This is the title of a manual of 156 pages devoted to the chemistry of the dairy, especially in respect of the manufacture of

butter and cheese, and the methods of feeding dairy cows. This book is a significant indication of the change which has taken place in the last few years among intelligent farmers and dairymen in regard to the methods of conducting their business. As a result of the education which has been given by the agricultural colleges and experiment stations, the dairy industry of this country is rapidly assuming a scientific character. The fact that a book such as the one which has been mentioned above can be printed and sold would be sufficient evidence of this, were it not seen also in the improvement in quality and the increase in quantity of dairy products. The book has been prepared with the object of furnishing useful information to a class of young men who intend to become farmers and dairymen rather than to scientific experts. The difficulty of preparing such a book is admittedly great, especially when written by a scientific man. It is hard to draw the line between a truly scientific exposition of a subject and the maudlin mouthings of kindergartenism. The author is to be congratulated upon having steered his course very satisfactorily between the Scylla of science and the Charybdis of baby talk. The intelligent dairyman is furnished with useful information in regard to the character of the products with which he is working, the methods of determining, in an approximate manner, their chief characteristics and the proper methods to be pursued in selecting dairy animals and feeding them for the highest product.

Chapter 2, on milk testing, Chapter 10, on sanitary conditions, and Chapter 14, on the effects of food upon dairy products, are of especial interest to dairymen.

A good book would not be quite perfect without some minor defects, and Mr. Snyder's work has not entirely escaped. One cannot see, for instance, why he describes the fat particles as "rubber balls," on page 2, and milk sugar as resembling "confectionery sugar without any sweet taste." In describing the amount of butter-fat in the solids of cream he states, on page 46, that it is from eighty to ninety per cent., while in the table giving the average composition of cream a simple computation will show that it is only seventy-seven per cent. On page 5 it is said that butter should contain about eighty-three per cent. of butter-fat, while on page 54 that num-

ber is given as its minimum content. The spelling of lactocrite and Feser, on pages 112 and 113, might be improved, as likewise the grammar in such a phrase as "there is rarely less than 12 pounds," on page 3. These are minor defects which the author will not fail to correct in a second edition, which, from the excellence of the work, will doubtless soon be demanded.

THE CONSTANTS OF NATURE. PART V. A RECALCULATION OF THE ATOMIC WEIGHTS. BY FRANK WIGGELSWORTH CLARKE. New Edition. Revised and enlarged. City of Washington. Published by the Smithsonian Institution. 1897. 8vo. vi + 370 pp.

The first edition of this work was published in 1882. Since then, and partly, no doubt, incited by that publication, a great deal of very excellent work upon atomic weights has been done. The appearance of Professor Morley's classical work on the relative atomic weights of oxygen and hydrogen has, especially, rendered possible a new calculation based on the hydrogen unit which will command universal acceptance among chemists. The present work is carried out on the same lines and with the same painstaking accuracy as the first edition. The exact means by which the final result is obtained is given in each case. While in the selection of the final value for each element due weight is given to chemical as well as mathematical evidence, there is also given for each the result of the purely mathematical combinations obtained by weighting each observer's value in accordance with the probable error. The comparative worthlessness of the probable error as showing the value of an atomic weight determination, and the necessity of considering chemical evidence as well, in spite of the objectionable "personal equation" introduced, is well shown by the fact that the probable error for oxygen as given by Professor Clarke in 1882 was 0.0035, while the present value differs from that then given by more than twenty-four times that amount.

The present work is, undoubtedly, the best available summary of our knowledge of atomic weights. W. A. NOYES.

TABLES FOR IRON ANALYSIS. BY JOHN A. ALLEN. vii + 85 pp. New York: John Wiley and Sons. Price $3.00.

The author states in his preface that serious discrepancy only exists in the atomic weights of magnesium and silicon, and, in

iron laboratories, these are used only for the determination of constituents which occur in small quantities. The amount of silica in slags and magnesia in slags and dolomitic limestones does not accord with this statement. A difference in the atomic weight of magnesium would also affect the determination of phosphorus as magnesium pyrophosphate. The commas should be omitted from some of the tables, and if they were arranged for one gram of sample and to cover larger percentages, they would be more valuable and much simpler.

More examples should be given to illustrate the manner of using the tables. Table XL should be headed "Factor Weights," and Table XLI "Atomic Weights." The tables are undoubtedly of value, but the arrangement might be much simplified. EDWARD K. LANDIS.

INORGANIC CHEMICAL PREPARATIONS. By FRANK HALL THORP, PH.D. 238 pp. Boston: Ginn and Co. Price $1.60.

In this book are found directions for the preparation of nearly one hundred compounds. Naturally enough, the salts of sodium, potassium, aluminum, ammonium, and iron receive the greater attention, but the remaining preparations are numerous and well selected, although no element is found among them.

The introductory remarks concerning solution, precipitation, filtration, evaporation, etc., are clear, full, and satisfactory, and the directions are, in most instances, all that could be desired. In some cases, however, the methods given would not furnish chemically pure substances.

Nearly all questions, that a student might ask, are anticipated and answered, while the use of equations to explain the chemistry of the methods and the incorporation in the text of numerous tables of solubility and specific gravity add not a little to the usefulness of the book.

In an appendix are placed specific gravity tables of the more common acids and ammonia, and a table showing atomic weights and valence.

The paucity of books of its kind and quality in the English language makes its appearance most welcome. L. B. HALL.

NITRO-EXPLOSIVES. By P. GERALD SANFORD. 8vo. 270 pp. 54 Illus. London: Crosby, Lockwood and Son. 1896. Price, 9 shillings.

The sub-title states that this book is a "Practical treatise con-

cerning the properties, manufacture, and analysis of nitrated substances, including the fulminates, smokeless powders and celluloid." A treatise to be practical should be first of all reliable, and second, it should be written in so clear and direct a manner that its descriptions may be easily and definitely understood by intelligent readers. The book before us is an example of the reverse of this, in that it is filled with errors and is so involved in its style that it is doubtful if any one but an expert could tell what it was that the author really sought to say.

As an example of the errors in the book we call attention to the description of the Boutmy & Faucher process of making nitroglycerine. This process is one of those best known to bookmakers; it has especially interested chemists, as its invention is believed to have arisen from the consideration of Berthelot's second thermo-chemical law; the invention was crowned by the French Academy; and the process has been repeatedly described, the reviewer having himself, as long ago as 1878, published an account of his visit to the works of the French Government at Vonges, where this process was operated, yet on page 16 of his book Mr. Sanford says, "A few years later (1872) M. M. Vouges and Boutnny* proposed to prepare nitro-glycerine by mixing the sulphuric acid with glycerine," etc., etc. The asterisk refers to the foot-note, "* *Comptes Rendus*, 75, and Desortiaux, *Traité sur la Poudre*, 684–686," and turning to the latter we read: "Le procédé employé depuis 1872 à la poudrerie des Vonges, et dû aux recherches de H. Boutmy et de L. Faucher," etc., etc. Throughout the book we find everywhere evidence of haste and negligence, so that one wonders why, if the author was unable to give the proper amount of time and effort to the preparation of the book, he should have undertaken it at all, and especially as no "long-felt want" existed for such a book.

The author states in his preface his belief "that the account given of the manufacture of nitroglycerine and of the gelatine dynamites will be found more complete than in any similar work yet published in this country," but a comparison with "The Manufacture of Explosives" by Oscar Guttman, published in London the previous year, shows that this earlier book devotes more than double the space to the treatment of these topics, and deals with them in a more systematic and thoughtful manner.

The chief merit of Sanford's book lies in the fact that he has collected and presented more information regarding analytical methods than is, to my knowledge, to be found in any one place, and if he had given his entire thought and attention to the elaboration of this material he would have produced a book of value and one which must have contributed to his professional reputation. As it is he has given us a crude work.

I am especially sorry to give this adverse opinion of his book, since Mr. Sanford quotes more freely from and oftener gives credit to American investigators than any other European writer on this subject.

CHARLES E. MUNROE.

A SIMPLE METHOD OF WATER ANALYSIS, ESPECIALLY DESIGNED FOR THE USE OF MEDICAL OFFICERS OF HEALTH. BY JOHN C. THRESH, M.D., D.Sc. 49 pages. 1897. Philadelphia: P. Blakiston, Son & Co., and London: John A. Churchill. Price 88 cents.

The book before us is one intended to so simplify the method of water analysis as to bring them within the power of the "Medical officers of health for rural districts" to accomplish, any such officer being "well aware that unless he himself can undertake the work it must remain undone."

The analytical processes described "require no specially fitted laboratory, and only the simplest possible apparatus," and the analysis "can be conducted in the neighborhood of the well or other source of supply."

The chemicals used are in the form of "Soloids" each containing exactly the requisite quantity, and they remind one of the "Fehling's Test" capsules now supplied to the medical profession.

That the book can fulfil any useful mission in this country is exceedingly doubtful. The processes described can give but approximate results at the best, and are such as would not be acceptable to a health officer were he a chemist, for the sufficient reason that he would be in a position to employ more exact methods. Should the officer in question not be a chemist he would be wise to omit analytical examination entirely, and content himself with a careful sanitary survey of the surroundings of the source of supply.

W. P. MASON.

THE COTTON PLANT.—ITS HISTORY, BOTANY, CHEMISTRY, CULTURE, ENEMIES, AND USES. Washington: Government Printing Office, 1896. 433 pp.

This is the title of Bulletin No. 33, issued by the Office of Experiment Stations of the Department of Agriculture. To all persons who are seeking for convenient and compendious information on this important plant, this bulletin will be of the greatest value. The parts which chiefly concern the readers of the Journal are the articles on the Chemistry of Cotton, prepared by J. B. McBryde and W. H. Beal, and the feeding experiments, by B. W. Kilgore. With commendable industry and research the compilers have brought together in convenient form for reference the analytical data scattered through journals and other sources, as a rule quite inaccessible to chemists at a distance from large libraries. The collated analyses treat of the entire plant, the roots, stems, leaves, bolls, lint, seed, hulls, oil, and seed cakes. The mean composition of the entire plant, of all its various parts, and of the products of its seed are given from all available data. The article on the feeding value of the seeds contains a résumé of the feeding experiments which have been conducted in this and other countries, arranged in such a manner as to secure in an easily accessible form the data of greatest importance. In this connection the reviewer would beg leave to suggest that the data relating to the injurious effects of feeding cotton-seed cakes to young animals would have had a greater value by being collected into a separate paragraph. Of particular interest to dairy chemists is the section relating to the effect of cotton-seed diet on the composition of butter.

In the article on the Chemistry of Cotton there is a paragraph relating to the carbohydrates of the cotton-seed which is hardly in harmony with the excellent character of the rest of the material and with our present knowledge of that subject. As is well known, the predominant sugar of the cotton-seed is raffinose and the described sugar, melitose, is now believed not to exist, or at least to be only an unstable union of raffinose with eukalyn. Repeated attempts of later and expert workers to isolate the so-called melitose from cotton-seeds have entirely failed. Tollens admits the term melitose as one of the synonyms of raffinose, but von Lippmann does not. On page 95

it is stated that Ritthausen describes "methods for separating melitose in crystalline forms, etc., and also gives some of its chemical and physical properties." Tollens, who reviewed the work of Ritthausen, established beyond question that these crystals were pure raffinose, and that the mythical substance, melitose, does not occur in cotton-seed, if it does exist in manna exuded from the *Eucalyptus viminalis and gunnii*. (*Ztschr. der Vereins für Rubenzuckerindustrie*, **35**, 591, and **36**, 217.)

Berthelot examined the Eucalyptus mannas above mentioned and gave the name melitose to the sugar they contained.[1] Subsequently he re-studied the material and came to the conclusion that his former statements were incorrect and he was convinced that melitose as such did not exist, but he kept the name for a preparation of raffinose from cotton-seed, which he secured in the cold, and which he supposed to be a very unstable compound with eukalyn.[2] No other investigator has ever been able to isolate this body and it is doubtless a myth. Even the existence of eukalyn is not certainly established. In the light of our present knowledge it seems that the term *gossypose* found on page 96 of the bulletin as an alternative name for melitose is the preferable characterization for this hearsay sugar.

BOOKS RECEIVED.

Bulletin No. 39. The Peach. Texas Agricultural Experiment Station, College Station, Brazos County, Texas. July, 1896. 48 pp.

El Kambio de Komposition ke Esperimenta el Agua de "el Salto." By K. Newman, Sandiego de Chile: Imprenta i Enkuadernazion. Proma. 1896. 14 pp.

Inorganic Chemical Preparations. By Frank Hall Thorp, Ph.D. iv + 238 pp. Boston: Ginn & Co. Price, $1.60.

Bulletin No. 42. I. Analyses of Manurial Substances sent on for Examination. II. Analyses of Licensed Fertilizers collected by the Agent of the Station during 1896. III. New Laws for the Regulation of the Trade in Commercial Fertilizers in Massachusetts. October, 1896. Hatch Experiment Station of Massachusetts Agricultural College, Amherst, Mass. 32 pp.

Physical Laboratory Manual for Secondary Schools. By Charles F. Adams, A.M. Chicago and New York: Werner School Book Co. 183 pp. 1896.

[1] *Ann. chim. Phys.* [3], **46**, 66.

[2] *Compt. rend.*, **103**, 533.